Final Report

Keeping Tahoe Blue:

Quantifying Atmospheric Nitrogen Oxides Upwind and in the Lake Tahoe Basin

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Report prepared for:

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January 2005

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Executive Summary

Observations of NO_2, total peroxy nitrates, total alkyl nitrates, and HNO_3 along with a variety of correlative measurements over the full annual cycle (March 2003- February 2004) were collected at Big Hill CA (38.842 °N, 120.408 °W, 1860 m). The elevation and location of the Big Hill site, approximately 30 km west of Lake Tahoe, were chosen so that observations made there could be analyzed to quantify the influence of urban areas, such as Sacramento and San Francisco, which are upwind of Lake Tahoe during westerly flow. Examining the seasonal and diurnal behaviour of reactive nitrogen at the site shows that in the *winter*:

- total reactive nitrogen is lower, net flow at the surface is downhill and the urban plume rarely reaches the western rim of the Basin

- individual episodes of high NO_2 and inorganic nitrates associated with small-scale burning events along the western slope may generate HNO_3 that can reach Tahoe

Combining our data with corresponding measurements at UC Blodgett Forest, we have developed a highly constrained model of the processes that govern reactive nitrogen distribution during the summer months in the region. Based on our analyses of the observations made, we can draw the following conclusions:

- During summer months, the Sacramento plume is the dominant source of reactive nitrogen in the region of the western slope of the Sierra Nevada, but this plume rarely reaches as far east as the Tahoe Basin

- HNO_3 deposition is sufficiently fast that very little remains in the plume by the time it reaches high elevation sites near the western rim of the Lake Tahoe Basin

- At Big Hill, similar concentrations of HNO_3 are found in airmasses coming from Sacramento (west) and Tahoe (east), demonstrating that urban areas to the west of Lake Tahoe cannot be identified as a net source of nitric acid to the Tahoe Basin

- Organic nitrates are significantly elevated in the plume compared to background conditions but their contribution to nitrogen deposition remains poorly understood

Yearlong measurements from Big Hill, just west of the Lake Tahoe Basin, show that the chemical processing, deposition, and dilution of urban emissions result in a negligible direct contribution of this upwind source to dry deposition of nitrogen oxides to Lake Tahoe.

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Keeping Tahoe Blue: Quantifying Atmospheric Nitrogen Oxides in the Lake Tahoe Basin

1. Introduction

Over the last 35 years, visibility in Lake Tahoe has decreased from 30 meters to 20 meters. Research suggests that a large part of this decrease is associated with increases in nutrient availability to microorganisms within the Lake. Both nitrogen and phosphorous are thought to be increasing. Nitrogen oxide and ammonia deposition to the Lake Tahoe basin and more broadly throughout the Sierra Nevada may have negative consequences associated with changing the nutrient balance and pH of lakes and streams. It may also alter ecosystem function by changing nitrogen-limited systems to ones that are saturated with available nitrogen. (Korontzi, Macko et al. 2000) show that nitrogen deposition to the forests of the San Bernardino Mountains, west of the Los Angeles Basin, has shifted the ecology in low lying regions from nitrogen limited to nearly nitrogen saturated conditions. They also report a correlation between nitrogen deposition and increased NO_3^- in the region's watersheds. These effects no doubt have parallels in the forests and hills downwind of the Sacramento metropolitan region including the site at UC-BFRS, the American River basin and possibly Lake Tahoe. Species-specific effects on California's ecology have also been the subject of discussion. For example, Keeley and Fotheringham (1997) argue that NO or NO_2 may be a signaling agent for seed germination in fire sensitive species. Downwind of urban areas, the implication is that many species may be perpetually germinating instead of germinating only after the clearing effects of fire. There are reports of direct uptake of artificially deposited organic nitrogen compounds (amino acids)(Nasholm, Ekblad et al. 1998), which raise the question of whether atmospheric organic nitrates might be directly assimilated either as nutrients or with toxic consequences. Recent work at the plant and leaf scale show that the mechanisms for nitrogen oxide exchange are complex and that there may be a compensation point controlling biosphere-atmosphere fluxes of some nitrogen oxides (Lerdau, Munger et al. 2000; Sparks, Monson et al. 2001). A compensation point is an atmospheric concentration below which nitrogen oxides are in the net emitted and above which they are, in the net, deposited to an ecosystem.

A large fraction of the input of nitrogen to Lake Tahoe is thought to occur by wet and dry deposition of atmospheric reactive nitrogen (both nitrogen oxides, collectively known as NO_y,

and ammonia) to surfaces within the Tahoe Basin. Atmospheric NO_y in the form of the chemical species NO and NO_2 (collectively known as NO_x), gas and particle phase nitric acid and gas and particle phase organic nitrates, each deposit to the materials on the Earth's surface (water, leaves, soils, etc) at different rates because of different solubilities and different reactivities. Further complicating the situation, it is known that NO, NO_2, and NH_3 are both deposited to and emitted from snow, soils and terrestrial plants depending on chemical and meteorological conditions at the surface and in the surrounding atmosphere. Emissions of species other than these three are possible--for example HONO emissions from surfaces are thought to be important to the OH chemistry of urban areas--but little is known about emission rates of other reactive nitrogen species. In the Lake Tahoe region, significant deposition of nitrogen oxides is thought to be occurring both directly to the lake surface and to the surrounding basin followed by runoff into the lake. Understanding the sources and the chemical speciation of nitrogen oxides in the atmosphere upwind of the Tahoe Basin is essential for evaluating models used to design control strategies aimed at reducing the nitrogen inputs to the Lake. Sources of atmospheric nitrogen oxides may include emissions from combustion, bacterial modification of fertilizers and natural bacterial emissions from the Sacramento Valley and the San Francisco Bay Area that are then transported to the Tahoe Basin, and/or emissions within the Tahoe Basin from vehicles and wood burning in stoves and fireplaces, and from bacterial sources in the soils and forests surrounding the lake.

Despite this wide range of policy relevant and scientifically interesting issues, the difficulty of accurately measuring nitrogen oxides and their deposition rates has prevented the development of an accurate, complete and detailed mechanistic understanding of nitrogen oxide deposition. This project was aimed at understanding the contribution of atmospheric nitrogen from west of the Tahoe Basin to the nitrogen oxide burden within the basin. Our goals were to provide to provide a detailed baseline of high time resolution observations of the annual cycle of 4 different types of reactive nitrogen oxides just to the west of the Tahoe Basin, to make those observations available to other investigators within ARB or elsewhere and to develop analyses using this data set. Further, we combine the Big Hill observations with data from our separately funded work at UC Blodgett forest and with data sets from other ARB investigators to provide a more quantitative understanding of the mechanisms and processes that establish the amount of each different nitrogen oxide species in the air to the west of the Tahoe basin. Our original

proposal called for measurements at the rim of the basin, which would have permitted direct evaluation of the composition of air at the ridge, providing insight into the speciation of nitrogen oxides within the basin. The ultimate location at Big Hill was to the west of that point due to overwhelming logistical difficulties associated with sampling within the basin, thus permitting only characterization of air outside the basin. Nonetheless the constraints developed from the data set provide a clear and convincing description of the contributions of transport from the west to the composition of air at the peak of the western slopes of the Sierra.

Prior work and outlook at the beginning of this study

Early on during the measurement period, we performed a review of the state of knowledge of transport along the western slopes of the Sierra and it effects on the nitrogen oxides arriving at the Lake Tahoe (attached in the appendix). That document provides a detailed review of the processes and mechanisms at work and of our understanding of the situation. It was completed about halfway through the measurement period and does incorporate some of the basic insights from our observations at Big Hill. None of the conclusions of that document are fundamentally altered by the final data, although much more detailed and quantitative analyses are now possible. We make no attempt to repeat the contents of that document here, but review them where necessary to understand the nitrogen oxide observations and their potential contribution to nitrogen deposition in the Tahoe Basin.

2. Measurement Sites

2.1 Big Hill Site

The Big Hill monitoring site (38.842 °N, 120.408 °W, 1860 m) is located in Eldorado National Forest in Placer County, California and was continuously maintained from March 2003 to March 2004. The site is located within a 24 000 acre forest fire scar from the Cleveland Fire of 1992. While some nearby areas have been replanted, there is minimal vegetation within 1 km of Big Hill (Figure 1). The site was approximately 5 km north of Highway 50 near the Union Valley Reservoir (Figures 2 & 3) and 30 km south west of Lake Tahoe. The road to the site was maintained during the winter by the Sacramento Municipal Utilities District, who operate a

communications tower at the top of Big Hill. An additional radio tower, a fire lookout and cabin, a helipad, and an outhouse comprised the other structures at the Big Hill site. A climate-controlled 9 m long trailer was used to house the trace gas instruments and was positioned on the west side of the hill, upwind of nearby structures during the daytime hours (Figure 4). Sampling inlets were mounted using a tower on the trailer roof, approximately 5 m above ground level.

2.2 Additional Measurement Site – UC Berkeley Blodgett Forest Research Station

The University of California operates a research site at Blodgett Forest (UC-BFRS) located about 20 km west of the Big Hill site. The coordinates are 38.88 °N, 120.62 °W at 1315 m elevation and the site is within a managed ponderosa pine plantation. Instruments are housed within a climate-controlled trailer and inlets are positioned at the top of a 10 m tower nearby. TD-LIF has been used to make measurements of reactive nitrogen at the site semi-continuously between October 2000 and the present. Additionally, long-term records exist for meteorological variables, CO_2, CO, ozone and several VOC. The main differences compared to Big Hill are that Blodgett Forest has significantly lower elevation, is 20 km closer to Sacramento, and is surrounded by dense vegetation. These factors have a dramatic influence on the meteorology and chemistry at the sites, and consequently on the partitioning of reactive nitrogen.

3. Instrumentation

The thermal dissociation laser-induced fluorescence instrument used to measure reactive nitrogen species makes possible simultaneous, rapid, cross-calibrated measurements of NO_2, peroxy nitrates, alkyl nitrates, and HNO_3. The details of this instrument and its performance characteristics during the Big Hill measurement campaign will be described below. In addition to the measurements of NO_{yi} species carried out by TD-LIF, CARB maintained a meteorological station to measure temperature, humidity and wind speed and direction. Inside the trailer, CARB had two beta-attenuation monitors (BAMs) to measure $PM_{2.5}$ and PM_{10}, and commercial instrumentation to measure NO_x, CO, and O_3. Data from these instruments was reported with one hour time resolution and to within the nearest ppb for NO_x and O_3. Chemical speciation data was

also collected using two week samplers. There were also time periods when a mini-sodar was operating at Big Hill to help in estimates of the boundary layer height in the region.

3.1 TD-LIF Instrument for NO_y

3.1.1 Thermal Dissociation Inlets

Thermal dissociation laser-induced fluorescence was used to make measurements of NO_2, the sum of peroxy nitrate species ($\Sigma PN \equiv RO_2NO_2$), the sum of alkyl nitrate species ($\Sigma AN \equiv RONO_2$), and HNO_3. Heated ovens thermally decompose the organic nitrates and nitric acid to NO_2 at temperatures characteristic of the compounds $XO\text{-}NO_2$ bond energy (Day, Wooldridge et al. 2002). At ambient temperatures, only NO_2 is responsible for the instrument signal. When the sample stream is heated to 180 °C for approximately 100 ms, the peroxy nitrates thermally decompose to yield NO_2. By subtracting the ambient NO_2 from the total NO_2 measured after heating, the concentration of peroxy nitrates can be calculated. In a similar fashion, the air stream is heated to 350 °C to dissociate alkyl nitrates and 550 °C for HNO_3. The TD-LIF instrument at Big Hill had two ovens so the ovens were cycled through temperature pairs to make measurements. Table 1 shows which NO_y species are measured as NO_2 for a given oven temperature, and how the oven temperatures are paired to arrive at measurements of individual groups of compounds. Figure 5 shows a diagram of the inlet system, which was housed in a 5 foot long, 4" x 4" steel box mounted to a tower on the trailer roof. The individual nitrogen oxide compounds (NO_{yi}) are converted to NO_2 immediately after entering the inlet to minimize sampling losses. Aside from the oven sections, which are made of quartz, all the tubing in the inlet system is made of PFA, including the 10 m long lines that delivered the air from the rooftop inlet to the instrument inside the trailer.

3.1.2 Laser-Induced Fluorescence

Laser-induced fluorescence is a highly sensitive and selective method for detecting NO_2 in the atmosphere (Thornton, Wooldridge et al. 2000). In the configuration used here, a Nd:YAG-pumped dye laser operating at 585 nm is used to excite a particular rovibronic feature in the NO_2 spectrum. The resulting fluorescence in each of two cells is collected by

photomultiplier tubes with laser scatter and background light being dramatically reduced by bandpass filters and time-gated detection. The sensitivity was also enhanced by use of a supersonic expansion in which the gas stream is expanded into low pressure (< 0.3 Torr) through a critical orifice. The resulting thermal cooling of the gas forces a greater fraction of the NO_2 molecules being sampled to absorb at the wavelength of light provided by the dye laser and results in a stronger fluorescence signal. Measurements were made at a rate of 1 Hz with an average detection limit throughout the campaign of 15 ppt/s.

3.1.3 Instrument Diagnostics

Careful effort was made to ensure the accuracy and precision of the measurements made by TD-LIF. A zero air generator (Sabio 1000) was used to provide clean air free of nitrogen oxides for zeros and calibrations. Zeros were performed approximately every two hours and were programmed to occur at every temperature setting. A NIST-traceable cylinder of 5.17 ppm NO_2 (BOC gases) was used for calibration of the instrument every three hours. Mass flow controllers (MKS) were used to dilute the NO_2 standard in zero air and deliver four known concentrations in the range of atmospheric concentrations. Zeros and calibrations were carried out by delivering the gas mix to the top of the inlet housing so that the gases would interact with the inlet in exactly the same manner as during routine sampling and with sufficient flow to overflow the inlet during these diagnostics. Furthermore, standard additions were carried out by adding a small flow of the NO_2 standard during sampling of the atmosphere to compare the instrument response and check for potential interferences resulting from atmospheric constituents. The conversion of peroxy nitrates, alkyl nitrates and HNO_3 to NO_2 enables us to calibrate using only NO_2 standards, however permeation tubes of n-propyl nitrate and HNO_3 were also used to check instrument response and, most importantly, to confirm oven temperature settings. As a result of these diagnostic procedures, the concentrations measured by TD-LIF are accurate to better than 10% for NO_2 and 15% for ΣPN, ΣAN, and HNO_3. Because it was necessary to cycle through oven pairs, measurement intervals for any compound were roughly 30 minutes, during which time data was collected at 1 Hz and could later be averaged for any desired time period. Figure 6 shows data acquired while sampling the atmosphere and slowly ramping the hotter oven (Oven 1) from a setting above Oven 2 to the same temperature. The y-axis shows that the

concentrations in both cells are on average the same when their temperatures are the same. The S-shape is consistent with the sample residence time in the oven and the known bond energies and unimolecular dissociation kinetics of the reactive nitrogen species being measured. Because there is no particle filter on the inlets, aerosol that comprises volatile nitrates (i.e. NH_4NO_3) thermally decomposes in the ovens yielding HNO_3, further decomposed to NO_2 only in the 550 °C oven. Therefore the values reported for the concentration of HNO_3 represent the sum of gas phase and semi-volatile aerosol nitrate. Laboratory studies have confirmed that the measurement does not capture non-volatile aerosol nitrate salts.

4. Results and Analyses

Measurements of the NO_y species NO_2, peroxy nitrates, alkyl nitrates and HNO_3 were made between March 2003 and February 2004 at Big Hill, whenever electricity was available to power the instrument. Despite being located in close proximity to the Sacramento Municipal Utilities District tower, power at the site failed frequently during the study, often during periods of bad weather. Meteorological variables, ozone, and PM were also measured and are incorporated into the analysis. The corresponding measurements made at Blodgett Forest will be included to develop a more complete picture of the factors controlling the distribution of reactive nitrogen within the region. The annual cycle of measurements will be discussed with reference to seasonal differences and their causes. Then the summertime data (June through October) will be analyzed more fully to examine correlations between trace gas constituents and climate variables.

4.1 Regional Transport

Due to its position on the western slope of the Sierra Nevada, Big Hill is subjected to extremely regular wind patterns, especially during the summer. Daytime heating causes upslope flow, which draws air from California's Central Valley eastward into the higher elevations of the Sierra Nevada range. When the sun sets, the flow reverses and the air drains from higher elevations back toward the valley floor. This flow regime persists along much of the western

slope of the Sierra Nevada and strongly influences the seasonal and diurnal patterns observed in primary and secondary pollutants seen in the region.

Figure 7 shows the location of Big Hill with respect to the nearby city of Sacramento and identifies many other air quality monitoring sites in the vicinity that sample air from the urban plume. Wind speed and direction measurements made at Blodgett Forest, Big Hill, and other Air Resources Board sites show that the general wind direction in the region is from the WSW during the day and the east at night. Blodgett Forest tends to experience winds from the NE at night while flow at Big Hill is from the SE, likely due to topographical differences between the two sites. Big Hill lies roughly 80 km from the eastern edge of the Sacramento suburbs, thus with an average wind speed of 15 km/h, it takes an airmass over 5 hours to reach the monitoring site. During the five hour transit time, the concentration of constituents within the urban plume may be altered by dilution, deposition, photochemical transformations and further emissions. Constraining a simple Lagrangian model using measurements made at sites along the Sacramento – Lake Tahoe transect allows us to separate out these parameters and identify the variables controlling nitrogen oxide concentrations in the Sierra Nevada foothills downwind of Sacramento.

It should be emphasized that observations made at these ground sites reflect the processing of boundary layer airmasses during the daytime. Evidence that will be described later shows that at 1850 m elevation, Big Hill frequently experiences nighttime downslope flow from the free troposphere. Figure 8 is a depiction of the region with the topographical features highlighted. The boundary layer, shown as the dotted line, is expected to be surface-tracking, at least to elevations of 2000 m in the daytime, and is significantly shallower at night. Flow near the surface follows arrows 1 and 2 with the second arrow dotted and bi-directional to represent the fact that once the sun sets, the flow reverses. Air that is lofted above the Central Valley (arrow 3) will likely be carried eastward with the prevailing winds (arrow 4). Both of these trajectories can bring airmasses that have received urban emissions of NO_x toward the Lake Tahoe Air Basin. In the case of surface flow, observations suggests that the wind rarely blows upslope hard enough and for a sufficient number of hours to deliver a species emitted in Sacramento to the Lake Tahoe Air Basin in the same day. Air masses following higher altitude paths may move further to the east in a given day but there must subsequently be a mechanism for that air to mix downwards in order for it to interact with the lake surface (arrow 5).

Figure 9 shows our calculations of the net weekly east-west airflow for a full year at Camino, based on wind speed and direction measurements at a California Irrigation Management Information Systems (CIMIS) site. Camino is close to Highway 50 between Blodgett Forest and Big Hill. The data suggests the while net airflow between March and October is from west to east, during the winter months long periods of downslope flow result in the net direction of flow at the surface being from Lake Tahoe toward Sacramento. During the winter, daytime upslope flow is generally too short-lived to transport anthropogenic pollutants from the Central Valley significantly further east than Big Hill. This analysis does not take into account the effect of transport aloft or the inclusion of pollutants into storm systems, which tend to move rapidly from west to east during the winter months.

On an average midsummer day, an airmass moves roughly 100 km from east to west while the sun is up and then may backtrack 40 km to the west overnight when the flow is reversed. This pattern results in air sloshing back and forth along the western slopes of the Sierra and significantly increases the regional background of reactive nitrogen. At lower elevation sites, like Blodgett Forest, airmasses measured at night were likely also sampled several hours earlier when they passed by in the opposite direction. At Big Hill, after midnight the lower abundance of H_2O and NO_y in the air suggests that the site is experiencing descending air characteristic of the free troposphere.

4.2 Seasonal Cycles in Nitrogen Oxide Species

Data was obtained at Big Hill for a full annual cycle from March 2003 – February 2004, allowing us to compare meteorology and reactive nitrogen for all the seasons. Figure 10 presents observations of temperature, absolute water vapour, and total reactive nitrogen NO_y ($\equiv NO_2 + \Sigma PN + \Sigma AN + HNO_3$). The absolute water vapour value is a mole fraction (reported in parts per thousand or o/oo) and represents the fraction of molecules in a volume of air which are water molecules. Relative humidity is then the ratio of the actual absolute humidity to the highest possible, or saturation, absolute humidity, which depends on the temperature of the air parcel. From the temperature data, it seems reasonable to consider two different sets of conditions: summer (June through October) and winter (November through April). Because of power delivery problems virtually no data was collected during May 2003. While the relative humidity

was quite low during the summer months, the absolute water vapour content is actually higher on average during summer compared to winter. Reactive nitrogen is higher during the summer months at the site though there is substantial day-to-day variability. Most notable perhaps is that the lower values, generally measured during the early morning, reach down almost to zero during the winter but generally not below 0.5 ppb in the summer. This seasonal cycle is consistent with corresponding measurements carried out at Blodgett Forest from 2001-2003. While emissions of precursor NO_x are not known the change substantially in the region by season, what does change is the extent to which these urban emissions are processed and transported to the western slope of the Sierra. As discussed above, net surface flow during the winter months is actually from east to west, so reactive nitrogen does not have the same opportunity to build up in the region that it does in the summer. The seasonal cycle in NO_y at Big Hill and Blodgett Forest is very different than that observed at sites that do not have a seasonal cycle in transport patterns. For example, Harvard Forest continues to sample air from urban sources to a similar extent throughout the year. During winter, lower rates of oxidation reduce the conversion of NO_2 to HNO_3, the ultimate sink of NO_y, and therefore maximum NO_y values are measured during the winter months (Munger, Wofsy et al. 1996; Moody, Munger et al. 1998). Another feature of the sites on the western slope of the Sierras that distinguish them from east coast sites is that almost all the precipitation falls as snow, thus wet deposition only acts as a sink of NO_y during the winter.

Figure 11 displays the full annual record for all the individual NO_{yi} compounds measured by the TD-LIF technique. The organic nitrate species, $RONO_2$ and RO_2NO_2 clearly maximize during the summer months, when higher temperatures and photochemical activity result in increased precursor VOC emissions, more rapid photochemistry and more persistent transport. HNO_3 is also generally higher during the summer months, averaging around 0.5 ppb, but higher excursions tend to occur during the winter months. NO_2 has the least clear seasonal cycle, likely because of compensatory effects between transport and chemistry. During the hot summer months, strong transport of urban emissions to remote high-elevation sites is offset by rapid photochemical oxidation of NO_x to NO_y. In the winter, the plume will have barely reached the site before downslope flow will carry the urban influence away but a much greater fraction of the total NO_y will remain as NO_2 due to reduced photochemistry.

Many of the winter season high NO_y events, especially in November 2003, occurred during prescribed burning events carried out by the US Forest Service or Sierra Pacific

Industries, who own much of the nearby forests. Smoke plumes could also be seen from apple orchards and vineyards near Pollock Pines. During these nearby burning events, NO_2 and HNO_3 were the most substantial contributions to NO_y and particulate nitrate was likely an important constituent based on data from the BAM and two week samplers. Some of the low values measured during the winter are the result of precipitation events that scrub soluble forms of NO_y, such as HNO_3, from the atmosphere.

4.3 Summer and Winter Timelines

In this section a summer week and a winter week will be examined in more detail to look at the variability in meteorological conditions and reactive nitrogen and ozone concentrations observed at Big Hill. Figure 12 shows meteorological data from a typical summer week that starts with hot dry conditions, with a cooler wetter weather pattern moving in on day 232. The pattern of upslope – downslope flow is dominant on all days except the day of the weather shift. Daytime winds are close to 4 m/s, while at night wind speeds average around 1 m/s and are more variable in direction.

Figures 13 and 14 show the observations of ozone, total NO_y and the individual NO_y species for the same time period. The late afternoon maximum is consistent with transport of urban pollutants by daytime upslope flow along the western Sierra slopes. Interestingly, while NO_2 and ΣPN exhibit the characteristic afternoon peak on day 230, it is noticeably absent in both O_3 and ΣAN, a co-product of ozone. In general, the patterns of NO_y and O_3 track each other during the summer months. HNO_3 is the only NO_y compound which remains as abundant during the cooler, wetter conditions at the end of the week. While total NO_y values do not decrease significantly at the end of the week, ozone is close to 30 ppb, and there is little apparent photochemical production.

Figure 15 shows the same meteorological variables as Figure 12, but for a week in late November. Winter conditions are less consistent than during the summer, but this data does demonstrate some widespread features in the data collected during the winter at Big Hill. The weather is cooler and the relative humidity is higher during this time period. Several days of strong flow from the southwest are interrupted on day 324 with a return to the more common upslope – downslope pattern but with weaker winds. Figure 16 shows that the diurnal variability

of ozone has diminished significantly and values for the week all lie between 45 and 65 ppb. Ozone is no longer correlated with NO_y, which is likely influenced by burning events during days 322-324. Figure 17 shows that strong flow from the west delivered high concentrations of NO_2, HNO_3 (and likely particulate nitrate) to the Big Hill site, which is likely due to plumes from upwind burning events. At the end of the weeklong period a diurnal cycle in NO_2, and especially ΣPN can be seen with the return to the usual flow pattern. Just as ozone concentrations have ceased to rise significantly above background values in the region, ΣAN remains very low throughout most of the winter.

4.4 Summertime Diurnal Profiles of Meteorology, Trace Gases and Particles

Figure 18 demonstrates the remarkably consistent meteorology experienced by the Big Hill site during the summer months (June through October in the following analysis). Temperatures were between 10 and 30 °C, with an average swing of approximately 7 °C between night and day. Rain was extremely rare and the relative humidity was generally between 25 and 50 %. With the exception of very few days, between roughly 9 am and 8 pm, the wind blows from the west. Wind direction during the night is more variable but is generally from the east or southeast. Wind speed maximizes during the afternoon at about 4 m/s, and is slowest in the early evening when the predominant flow is changing direction from upslope to downslope. Wind speeds during the night are more variable but are generally slower than during the day. We exploit the regularity of the transport and climate variables to analyze the data statistically and build up our understanding of the important parameters involved in determining NO_y distribution in the region.

Figure 19 depicts the diurnal cycles measured in ozone, particulate matter, and total reactive nitrogen. As a result of daytime flow from the valley toward the site, and the photochemical processing that occurs along the way, all three of these variables maximize around 6-8 pm, just before downslope flow begins. The minimum values in each of the variables occur around 10 am just after upslope flow has started.

The summertime diurnal cycles in the individual reactive nitrogen species are shown in Figure 20. HNO_3 has a remarkably flat diurnal profile at the Big Hill site, in contrast to measurements made by TD-LIF at both Blodgett Forest and Granite Bay, a Sacramento suburb. At those sites, the profile of HNO_3 followed that of the sun, peaking in the middle of the day and

decreasing to close to zero at night. The rationale behind the different pattern at Big Hill is two-fold: during the day HNO_3 at Big Hill is lower because the site is further from the NO_x source and the HNO_3 produced during plume transit has had more time to deposit, while at night HNO_3 is higher than other surface sites because it is sampling descending air characteristic of the free troposphere, in which the HNO_3 formed has not had the opportunity to deposit. An illustration of this effect can be found in Figure 21, a time series of absolute water concentration and the ratio of HNO_3/NO_y observed at Big Hill. Because the photochemical production of nitric acid does not occur at night, its rapid deposition to the surface would be expected to reduce its importance in the total amount of reactive nitrogen seen at night. This is seen at Blodgett Forest, however at Big Hill, the contribution of HNO_3 to NO_y grows in importance during the nighttime hours suggesting that the nighttime airmasses observed at this high elevation site have not been recently near the surface. Additionally, the water vapor mixing ratio frequently decreases abruptly shortly after midnight, suggesting that the site is experiencing mixing from above of drier airmasses that have less total NO_y but of which HNO_3 is a relatively important constituent.

Alkyl nitrates are formed photochemically through the association of peroxy radicals with nitric oxide. The RO_2 + NO reaction can also form ozone, hence the alkyl nitrate concentrations are generally a good indication of ozone production. Alkyls nitrates have also been observed to be well-correlated with carbon monoxide at remote sites (Flocke, Volzthomas et al. 1991; Shepson, Anlauf et al. 1993) however the CO monitor at Big Hill did not have sufficient sensitivity to make measurements during the campaign. Alkyl nitrates were at a minimum in the early morning and exhibited peak values in the late afternoon. TD-LIF measurements of alkyl nitrates at Blodgett Forest are similar to those at Big Hill, but both sites observe ΣAN values that are substantially larger than those reported by researchers measuring individual alkyl nitrates by GC-MS (Day, Dillon et al. 2003). Because the TD-LIF technique takes advantage of the characteristic bond energies of organic nitrates it does not require prior identification of specific organic groups and the measurements represent the sum of all RO_xNO_2 compounds in the atmosphere. The speciation of the alkyl nitrates observed at Big Hill is unclear, though the dominance of VOC reactivity by isoprene between Sacramento and Big Hill suggests that alkyl nitrates derived from isoprene products are likely important. The sinks of alkyl nitrates are poorly understood though their thermal decomposition and photolysis lifetimes exceed several days. The presence of hydroxy-groups or unsaturated bonds in the organic chain

may reduce the lifetime of a specific compound, though if it reacts to form another alkyl nitrate, it will not register as a loss of ΣAN as seen by the TD-LIF measurements. Measurements in the western Sierra region suggest that ΣAN are a significant fraction of NO_y and that they tend to be long-lived, suggesting that they contribute substantially to the reactive nitrogen that is exported from the region and mixed into the free troposphere. The ability of alkyl nitrates to deposit to surfaces and contribute to nitrogen deposition is poorly understood.

Peroxy nitrates have a substantial diurnal profile at Big Hill, peaking between 2 pm and 6 pm at values more than double those observed during early morning hours. ΣPN are formed through the association of a peroxy radical and nitrogen dioxide, but only those derived from acyl peroxy radicals are stable enough to survive in the atmosphere. The most common peroxy nitrate, peroxy acetyl nitrate (PAN), is the result of the photochemical oxidation of acetaldehyde in the presence of NO_x. Acyl peroxy nitrates act as a thermally labile reservoir for both RO_2 and NO_2 radicals and therefore on cooler days can sequester these radicals and reduce photochemical ozone production. Peroxy nitrates can also be responsible for transporting reactive nitrogen far from its original source, and act as a radical source upon subsequent decomposition. PAN is known to be acutely toxic to plants at high concentrations, but not much is known about the effects of chronic exposure at the ppb-level. Organic nitrates have relatively low water solubility and their contribution to reactive nitrogen deposition is not well understood.

Nitrogen dioxide also has a strong diurnal cycle and has the latest peak of all of the reactive nitrogen compounds at Big Hill. The delayed timing of the peak concentrations can be explained by a combination of transport and photochemistry. The NO_2 emitted into the plume takes around six hours to arrive at the Big Hill site. Air masses leaving Sacramento in the late morning are advected up the Sierra when photochemical activity is peaking, and the conversion of NO_x to higher NO_y species is maximized. Air leaving Sacramento in the afternoon and arriving at Big Hill in the early evening experiences lower levels of actinic radiation and therefore the later part of the plume has a larger fraction of NO_2 remaining. Peak concentrations in the plume are roughly double the early morning minimum values.

Figure 22 shows the partitioning of the NO_y budget at Big Hill by time of day. During the early morning hours, when the site experiences dry, clean air, characteristic of the free troposphere, almost 40 % of the NO_y is HNO_3, with the other three classes of compounds

contributing about 20 % each. At the height of the plume in the late afternoon, the contribution of HNO_3 has shrunk to 25 % and ΣPN have become more important. NO_2 never accounts for more than 25 % of the NO_y measured at the site and is most important near sun set. The contribution of ΣAN varies from 15 % of NO_y during the early morning hours to about 25 % in the evening. Peroxy nitrates are most important at the site during mid-afternoon, when they make up almost one third of the reactive nitrogen.

4.5 Summertime Distribution of Reactive Nitrogen and Correlation with Other Variables

Changes in climate can be expected to drive differences in both transport and chemistry, affecting the geographical and temporal extent to which the urban plume affects remote sites, and the chemical partitioning with the plume. One of the most important climate variables that governs the distribution of reactive nitrogen oxides is the temperature. The summertime data was divided into two sets of days, half of which had a maximum daytime temperature above 21 °C and half of which did not. The average amount of NO_y in the plume was 1.71 ± 0.04 ppb on cold days and 1.91 ± 0.04 ppb on hot days, suggesting that higher local temperatures may indicate a slightly stronger transport efficiency of the plume. The partitioning of reactive nitrogen among its constituent species is strongly influenced by temperature as shown in Figure 23. The top panel shows the partitioning among NO_y species arriving at the site between 1 pm and 8 pm on days when the maximum temperature exceeded 21 °C. Comparison with cooler temperature data displayed in the bottom panel shows that while NO_2 has undergone similar amounts of photochemical processing under both sets of conditions, lower temperatures favour the accumulation of peroxy nitrates over the production of alkyl nitrates. Peroxy nitrates account for over one third of the reactive nitrogen under the cooler temperatures, sequestering a substantial amount of reactive nitrogen in this reservoir. The reduced contribution of alkyl nitrates at lower temperatures is consistent with fewer RO_2 and NO_x radicals available to react to form ozone. Indeed, the mean ozone in the plume on the hot days is 64 ppb, while on cool days it is 58 ppb suggesting that temperature plays a crucial role in determining the availability to NO_2 for ozone production. Another facet of the temperature effect may be the increased emissions of many biogenic VOC at higher temperatures. A shift in the hydrocarbon composition toward longer

chain compounds as opposed to carbonyl compounds could favour the production of alkyl nitrates over peroxy nitrates.

In Figure 24, the correlation between total reactive nitrogen and the mole fraction of water is shown for the six days in August used for Figure 21. The relationship between H_2O and NO_y is not as clear at Blodgett Forest, where it is likely that the transpiration of nearby vegetation has a strong influence on the water budget at the site. In contrast, water vapour appears to be a good indicator of transport of polluted airmasses at a high elevation site such as Big Hill. Observations during the night show that the air descending from the free troposphere tends to be much drier and have reduced total reactive nitrogen. The slope and intercept of the correlation between the two variables changes over time but in general, the two seem to be correlated. The absolute humidity of the airmass records the degree of mixing that the relatively moist, polluted urban plume has undergone in transit to the high elevation site.

The implication of figures 21 and 24 is that nighttime observations at Big Hill allow us to occasionally sample airmasses which have not had recent contact with the surface. Recalling the diagram in Figure 8, these airmasses could be visualized as having traveled along arrow 4 during the daytime and subsequently descending to the surface and undergoing downslope flow along arrow 2 at night. These airmasses have lower concentrations of H_2O and NO_y than those that are observed during upslope flow and their concentrations likely reflect the degree to which earlier surface emissions have mixed with cleaner air from the free troposphere. While we observe these descending airmasses at a high elevation site on the western slope of the Sierra Nevada range, it is not clear if the same transport phenomenon occurs to bring air toward the surface of the Tahoe Basin. If so, this is a potential mechanism for delivering reactive nitrogen to the surface, but it should be stressed that while the fractional contribution of HNO_3 to NO_y was higher in these airmasses, the absolute concentration of HNO_3 was no higher than in the daytime plumes.

Figure 25 depicts the remarkable correlation between reactive nitrogen and ozone at the Big Hill monitoring site throughout the summer. Observations made during afternoon upslope flow are highlighted in orange and show that higher values for ozone and NO_y occur when the urban plume is influencing the site. Other high values are measured shortly after the wind has shifted direction and the air passing back by the site is still characteristic of plume air. The relationship between NO_y and ozone is expected because both are derived from precursor

emissions of nitrogen oxides. While in urban areas with high NO_x concentrations, ozone can be anti-correlated with NO_x, in remote areas like Big Hill we expected ozone production to be limited by the availability of nitrogen oxides. Minimum values of NO_y (< 1 ppb), which occur in the early morning hours, are associated with ozone levels between 35 and 60 ppb, while maximum values of NO_y (> 2.5 ppb) are associated with ozone between 65 and 95 ppb. Clearly the chemistry and transport patterns responsible for transforming nitrogen oxides and transporting them the western slope of the Sierra have similar effects for ozone and total reactive nitrogen.

A great deal of insight can be gained by comparing observations made at Big Hill to corresponding measurements at the Blodgett Forest site. As mentioned above, both sites lie along the Sacramento – Lake Tahoe transect, but Big Hill is at a higher elevation, a greater distance from the city, and has less vegetation and cooler temperatures. Our analyses of the diurnal cycles at the two sites suggest that they sample similar airmasses during upslope flow and we restrict the comparison the times between 1 pm and 8 pm when both sites are strongly influenced by the Sacramento urban plume. Figures 26 a-f show the normalized probability distributions for the individual reactive nitrogen species, total NO_y and O_3 for both the Big Hill and Blodgett Forest sites. In the case of NO_2, Big Hill values (median 0.25 ppb) are on average less that half those of Blodgett Forest with significantly fewer half hour periods with more than 1 ppb. This means that the dilution and photo-oxidation of NO_2 in the plume is quickly reducing its concentration several hours downwind of Sacramento. In this region, ozone production is expected to be NO_x-limited so it can also be inferred that instantaneous ozone production rates drop off quickly between Blodgett Forest and Big Hill.

Peroxy nitrates have a wider probability distribution at Blodgett Forest than at Big Hill and higher median observations. While absolute ΣPN concentrations are higher on average at UC-BFRS, the ratio of peroxy nitrates to NO_2 is actually higher at Big Hill, likely due to the lower temperatures, stabilizing the reservoir species. This confirms that as the plume is advected, it is being significantly diluted with air that has less NO_2 and ΣPN, and that the photochemical oxidation of NO_2 to peroxy nitrates acts as a permanent sink of NO_x when temperatures are cool. The probability distributions of alkyl nitrates are extremely similar at the two sites, but for different reasons. The breadth in the distribution at Big Hill derives from a stronger diurnal cycle

whereas than at Blodgett Forest, where it appears to result from more day-to-day variability. Nevertheless, detailed comparison of the observations of alkyl nitrates at the two sites suggests that as a group these compounds are lost very slowly to deposition but are diluted when mixed with air from the free troposphere. Correlations between alkyl nitrates and CO and O_3 show that they are associated with polluted, upslope air and are formed in conjunction with ozone during photochemical activity. The deposition of most alkyl nitrates appears to be slow enough that a substantial fraction of what is produced in the plume stays in the atmosphere. From the perspective of nitrogen deposition, not enough is known about the behaviour of these compounds at the surface.

The fact that HNO_3 concentrations are similar, regardless of the wind direction at Big Hill suggests that there is no significant advection of HNO_3 from Sacramento to the Lake Tahoe Air Basin. In other words, there is a negligible net flux of HNO_3 from west to east along the surface of the Sierra range. HNO_3 concentrations are lower and less variable at Big Hill compared to Blodgett Forest. However, similar to the peroxy nitrates, if considered in a relative sense, HNO_3/NO_2 in the plume is higher at Big Hill. The flat diurnal profile for HNO_3 at Big Hill suggests that this site is far enough from fresh NO_x sources that much of the HNO_3 produced during oxidation has already had the chance to deposit before reaching high elevation sites at the surface. Blodgett Forest has higher daytime NO_2 concentrations capable of generating strong local production of HNO_3, but HNO_3 production at Big Hill is less efficient both because the plume is more dilute and because lower temperatures lead to the sequestration of NO_2 by peroxy nitrate formation.

The distribution of total NO_y at the two sites reflects the proximity of Blodgett Forest to Sacramento in both the higher average and the greater variability in concentrations. At Blodgett Forest, the total NO_y in the plume varies between 1-5 ppb, whereas at Big Hill it ranges from 0.5-3.5 ppb. The data used in this analysis was not limited to days on which there was persistent upslope flow, thus some of the lower numbers likely result from days on which the urban plume did not influence the site. The greater variability in total NO_y compared to any of its constituent species shows that the variability in NO_{yi} is governed by the extent to which the total urban emissions are influencing these remote sites rather than by differences in partitioning among the available reactive nitrogen. It is not clear from the local meteorological observations, aside from

wind direction, which conditions result in higher concentrations of reactive nitrogen being transported in the boundary layer along the western slope of the Sierra.

Finally, the distribution of ozone within the urban plume is shown for each site in Figure 26f. Remarkably, the median ozone concentration at each site is very similar, but Blodgett Forest shows both more low values and more high values. The similarity between the two sites results partly from the fact that daytime ozone values are generally not more than a factor of two higher than the regional background, so mixing with the background drives concentrations toward a common value. From a regulatory standpoint, the Blodgett Forest site is much more likely to exceed the federal 8 hour ozone standard because of the significantly higher number of observations above 85 ppb. Comparison of ozone at the two sites suggests that the efficiency of ozone production has slowed considerably by the time the plume has reached Blodgett Forest, and it can no longer match the decreases in ozone due to dilution and deposition as the air moves toward Big Hill. This information can be used to ascertain the extent of influence of the urban plume on ozone in the region.

4.6 Observational Constraints on the Transport of Nitrogen Oxides

Table 2 compiles data from the probability distributions shown in Figure 26 for the Blodgett Forest and Big Hill sites. Because the data sets are comprehensive and the meteorological conditions are extremely regular, it is possible to treat the data statistically. We have combined these data sets, along with observations made in the summer of 2001 at Granite Bay, a suburb of Sacramento near Folsom, to constrain a Lagrangian model of the plume that includes photochemistry, deposition, dilution, and emissions as it is advected eastward from the urban area over the western slopes of the Sierra. Figure 27 shows measurements of the NO_2 and total NO_y (given as NO_x at the urban locations) as the air moves along the Sacramento – Tahoe transect. Concentrations were averaged for different time periods depending on the location, reflecting the Lagrangian nature of the analysis, and using observed wind speeds to establish the transit time of the plume.

Using observations of anthropogenic VOC from Granite Bay and Blodgett Forest in 2001, we have confirmed the estimate for a dilution rate of approximately 0.25 h^{-1}, found by Dillon et. al. (2002). Analysis that includes measurements of NO_2, ΣPN, ΣAN, HNO_3 and O_3, constrains rates of further NO_x emissions, photochemical oxidation and deposition within the

plume as it is advected along the western slope of the Sierra. HNO_3 production is most efficient at the high NO_x concentrations of Sacramento, but as the plume advects eastward and biogenic emissions of VOC are added, the production of organic nitrates begins to compete for NO_x. Between Folsom and Blodgett Forest there are relatively high levels of production of all forms of NO_z ($\equiv \Sigma PN + \Sigma AN + HNO_3$) because of the optimal balance between NO_x and RO_x precursors. Comparison of Blodgett and Big Hill data suggests that the fate of ΣPN depends on the temperature, that ΣAN are well-conserved within the plume, and that deposition of HNO_3 is the most important sink of total reactive nitrogen. The lifetime to deposition of HNO_3 in the plume is estimated at less than five hours and since most of the production occurs close to the city, a considerable amount of the HNO_3 present in the plume has been lost before it arrives at Big Hill. Our observations indicate that a substantial amount of mixing occurs across the boundary between the surface layer and the free troposphere, which implies that the plume is responsible for exporting substantial amounts of reactive nitrogen that can be transported above the continent at high altitudes. Clearly, local emissions from South Lake Tahoe dominate over the contribution of the processed and diluted reactive nitrogen present in any airmasses that may reach the Tahoe Basin. To quantitatively assess the relative importance of upwind transport and local emissions in the Basin as a whole would require analysis of measurements from other Tahoe sites further from roads and other intense NO_x sources.

5.Conclusions and Implications

The motivation for collecting data at Big Hill and the focus for this analysis has been to quantify the distribution of reactive nitrogen oxides at a site upwind of Lake Tahoe and use those measurements to assess the role of transport along the western slope of the Sierra in contributing to nitrogen deposition in Lake Tahoe. By combining the data we obtained at Big Hill with corresponding measurements at Blodgett Forest, we have developed a highly constrained model of the processes that govern reactive nitrogen distribution during the summer months in the region. Data collected during winter months show that the meteorology does not favour net transport of pollutants from west to east in the surface layer. Plumes from several prescribed burns were measured, often containing higher concentrations of reactive nitrogen than the urban plume, but likely having significantly reduced geographical influence. Total reactive nitrogen in

the region is likely at a maximum during the summer, though observations from more sites would be necessary to quantify the importance of burning events as a source of reactive nitrogen to Lake Tahoe. Based on our analyses of the observations made, we can draw the following conclusions:

- During summer months, the Sacramento region is the dominant source of reactive nitrogen in the plume on the western slope of the Sierra Nevada

- HNO_3 deposition is sufficiently fast that very little remains in the plume by the time it reaches high elevation sites near the western rim of the Lake Tahoe Basin

- At Big Hill, similar concentrations of HNO_3 are found in airmasses coming from the west and the east, suggesting that urban areas to the west of Lake Tahoe cannot be identified as important sources

- Organic nitrates are significantly elevated in the plume compared to background conditions but their contribution to nitrogen deposition is poorly understood

- During winter months, total reactive nitrogen is lower, net flow at the surface is downhill and the urban plume rarely reaches the western rim of the Basin

- Individual winter episodes of high NO_2 and inorganic nitrates associated with small-scale burning events along the western slope and may generate HNO_3 that can reach Tahoe

6. References

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7. Tables

Oven Temp (°C)	NO_2 Signal From	Temperature Pairs	Species Measured
30	NO_2	30, 180	NO_2, ΣPN
180	NO_2, ΣPN	180, 350	ΣAN
350	NO_2, ΣPN, ΣAN	350, 550	HNO_3, NO_y
550	NO_2, ΣPN, ΣAN, HNO_3		

Table 1. Oven temperatures and pairings used to measure individual types of NO_y species using the thermal dissociation laser-induced fluorescence technique.

	Blodgett Forest			Big Hill		
Species	Median (ppb)	5th percentile	95th percentile	Median (ppb)	5th percentile	95th percentile
NO_2	0.63	0.30	1.70	0.33	0.16	0.78
ΣPN	0.79	0.27	1.75	0.55	0.21	1.07
ΣAN	0.41	0.15	0.77	0.39	0.16	0.78
HNO_3	0.79	0.33	1.48	0.53	0.25	0.85
NO_y	2.68	1.57	4.92	1.84	1.05	2.99
O_3	61.5	40.7	88.4	60	45	82

Table 2. Data for June-October, 1 pm – 8 pm at Blodgett Forest and Big Hill. For each species listed the median, 5th and 95th percentile values have been calculated in ppb.

8. Figures

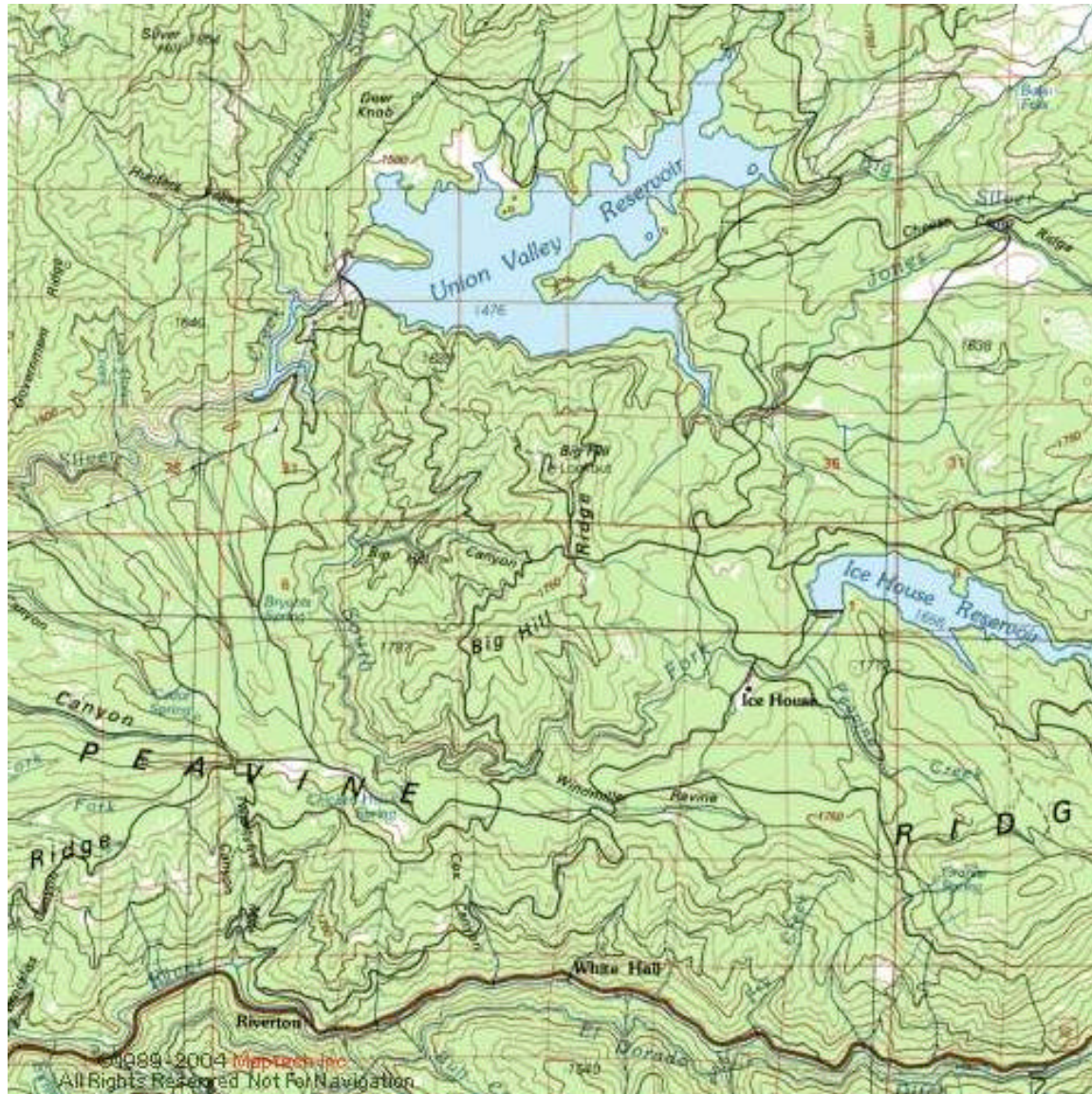Figure 1. View of Big Hill site from the west

Figure 2. Map of Crystal Springs area showing Union Valley reservoir just to the north of the Big Hill lookout site and Highway 50 at the bottom of the map.
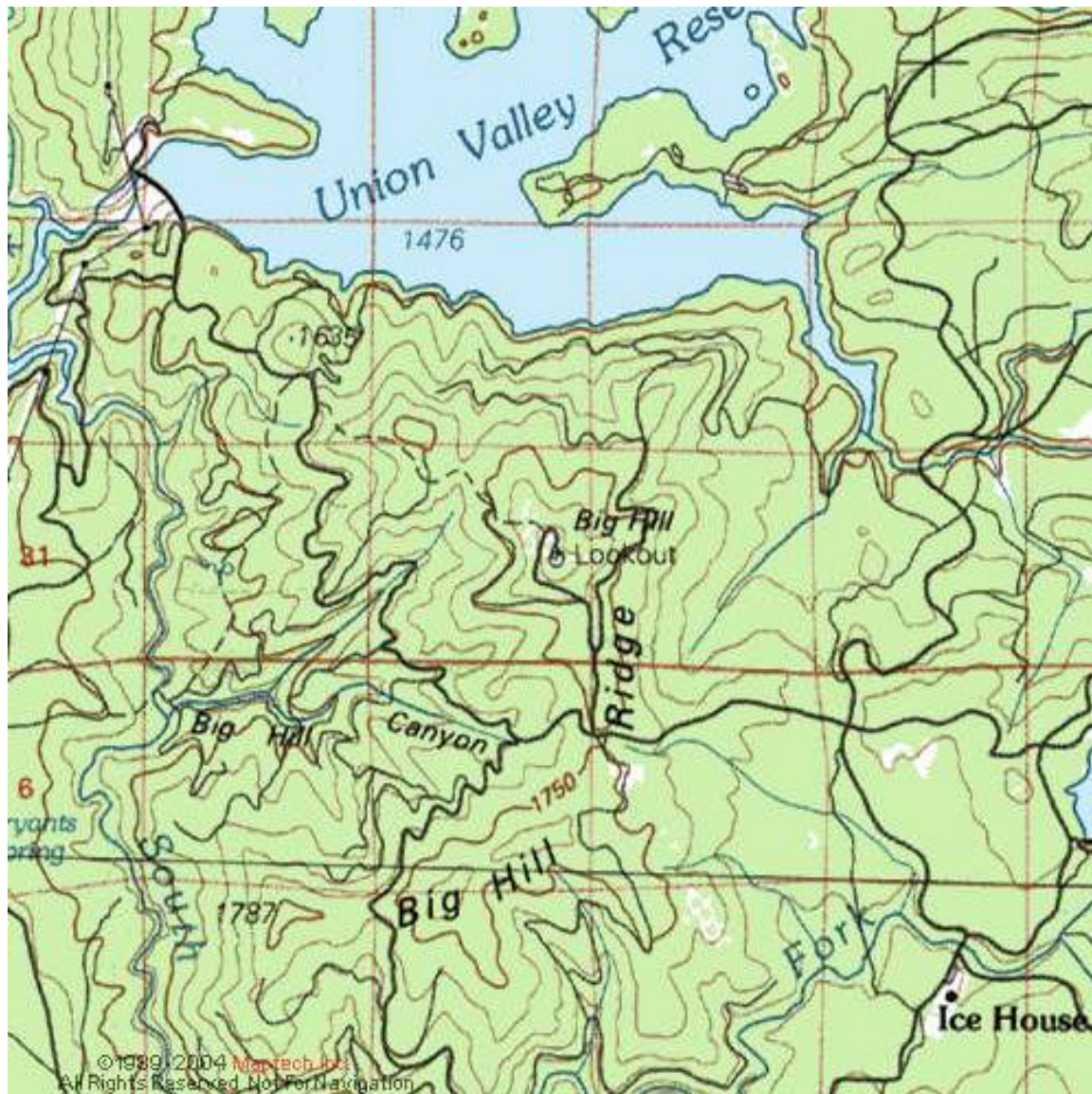
Figure 3. Higher resolution map of topographical features and roads in proximity to the Big Hill monitoring site.

Figure 4. Monitoring site at Big Hill showing two-week samplers, instrument trailer with in lets of roof , mini-SODAR and meterological station.
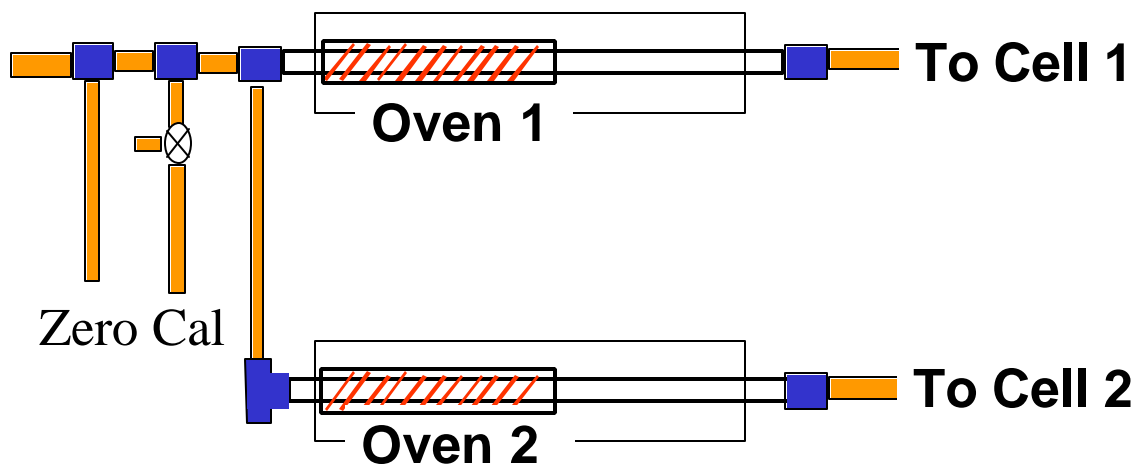
Figure 5. Diagram of heated inlets used to dissociate reactive nitrogen oxides to NO_2 prior to detection in the optical cells. The diagram shows the additions of calibration and zero air gases occur at the top of the inlet and travel the same sampling lines as the ambient gas being measured.
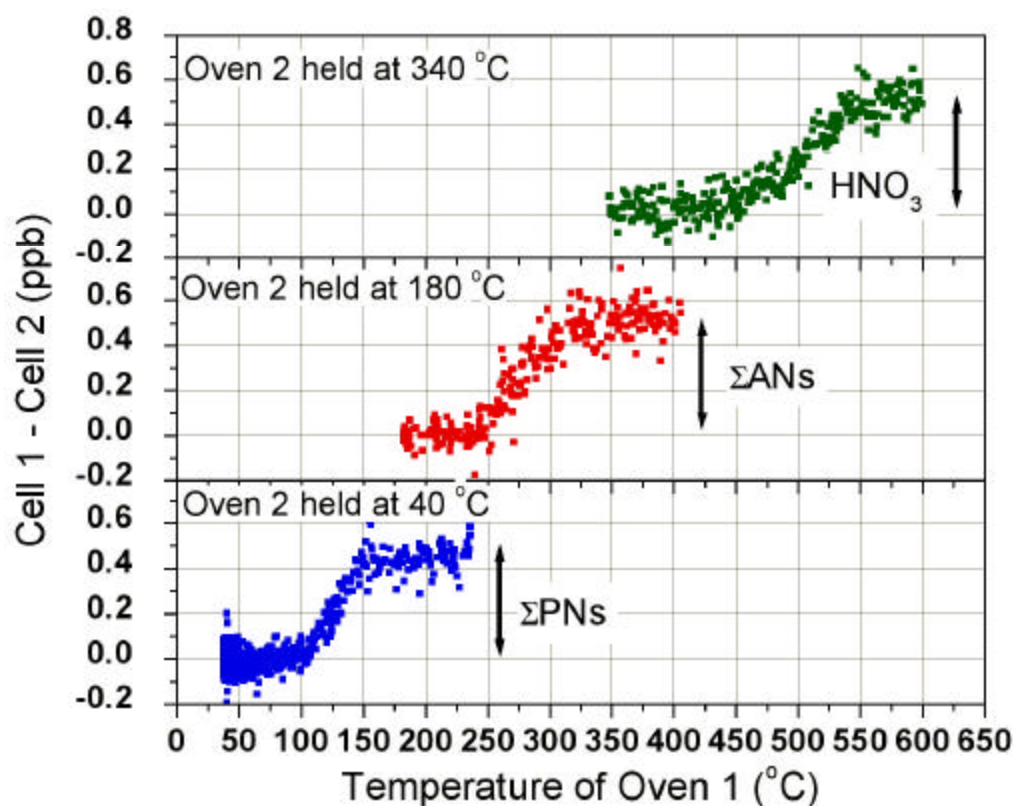
Figure 6. The y-axis shows how the difference in concentrations of NO_2 being measured in cells 1 and 2 changes as oven 1 is ramped from a temperature well above oven 2 down to the same temperature. For example the lower panel shows that the concentration difference between cells 1 and 2 can be attributed to peroxynitrates when their ovens are set to 180 and 40 C respectively. When the temperature of oven 1 is slowly reduced to be the same as oven 2 the two cells agree on average. Each datapoint represents a 3-second average during a scan of the ambient atmosphere.
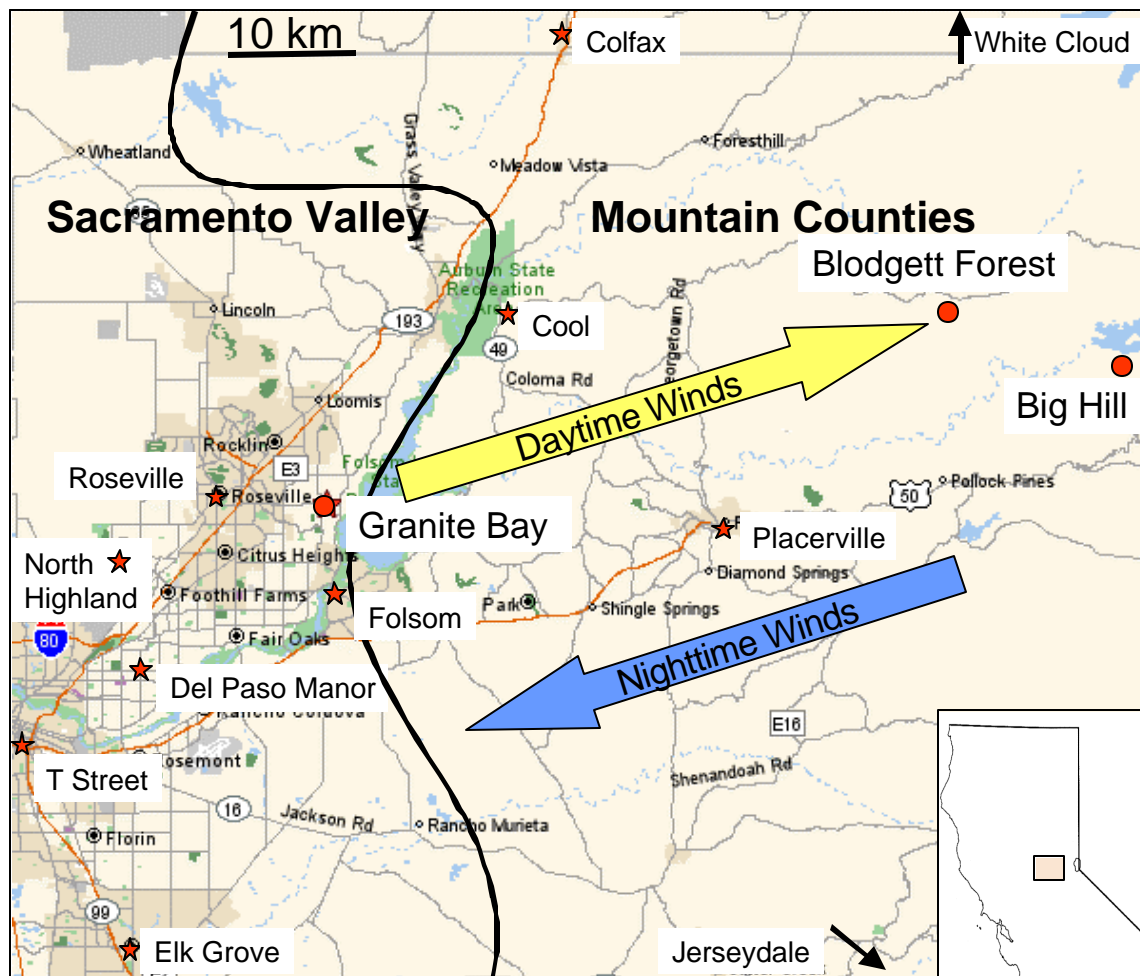
Figure 7. Map of Central California including air quality monitoring sites in portions of the Sacramento Valley and Mountain Counties air basins. Sites marked with stars are Air Resources Board monitoring sites, while sites marked with circles are sites where the UC Berkeley TD-LIF instrument has been deployed to make measurements of nitrogen oxide species. The dominant daytime and nighttime wind directions are depicted by the arrows and the inset shows the location of the region within the state of California.
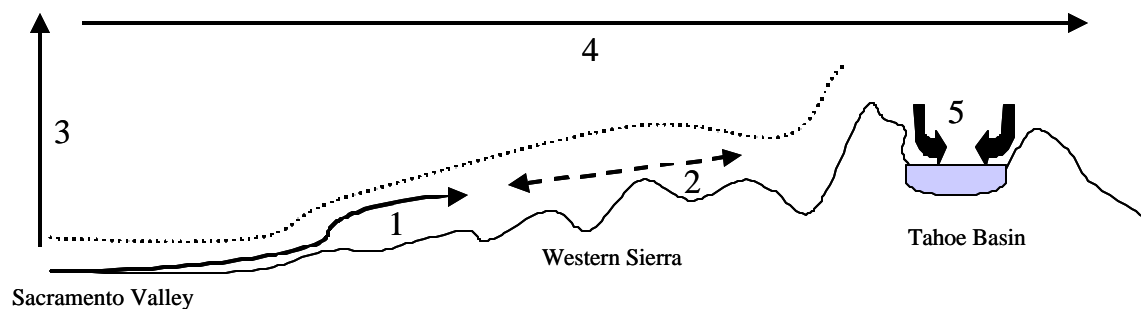
Figure 8. Topographical diagram of airflow along the western slope of the Sierra Nevada. Daytime boundary layer airmasses arriving in Sacramento and receiving urban emissions may be advected eastward near the surface undergoing dilution, chemistry, biogenic emissions and deposition along arrows 1 and 2. Alternately, some airmasses may be lofted high above the floor of the Central Valley and move eastward over the western Sierra disconnected from interactions with the surface (arrows 3 and 4). Airmasses that pass over the roughly 3000 m peaks to the west of the Lake Tahoe Basin or flow through canyons may subsequently be mixed downward and be exposed to the lake surface (arrow 5).
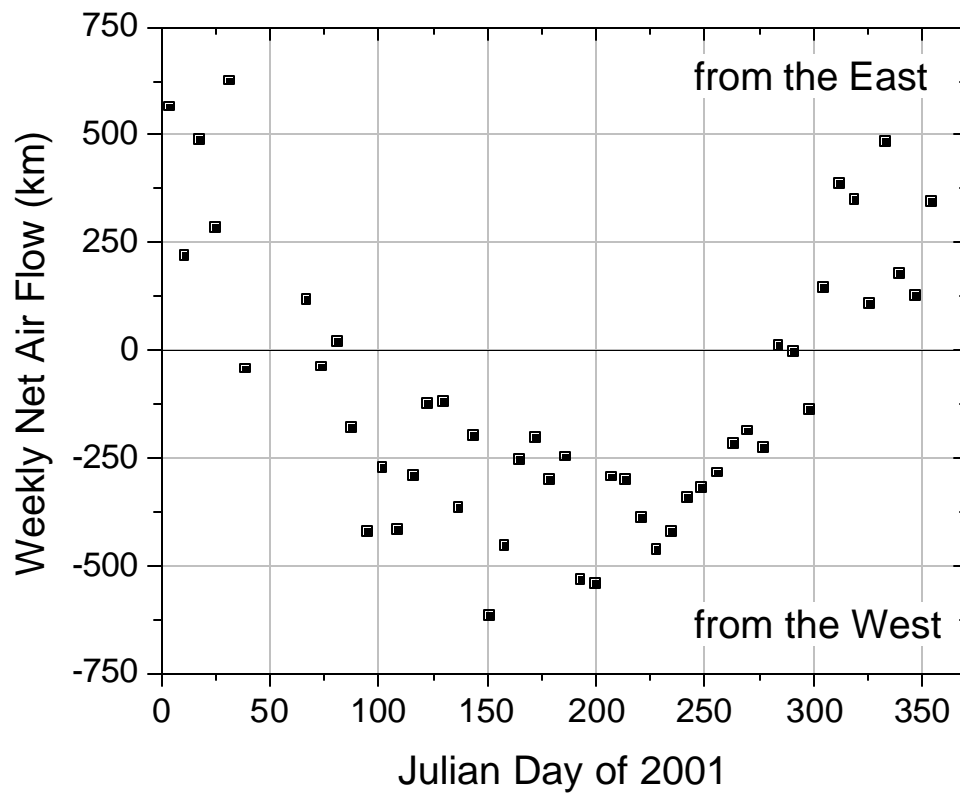
Figure 9. Depiction of regional weekly net airflow using meteorological data from the Camino CIMIS site close to Pollock Pines near Highway 50. Between March and October, net flow in the region is from west to east, however this trend is reversed during the winter months.
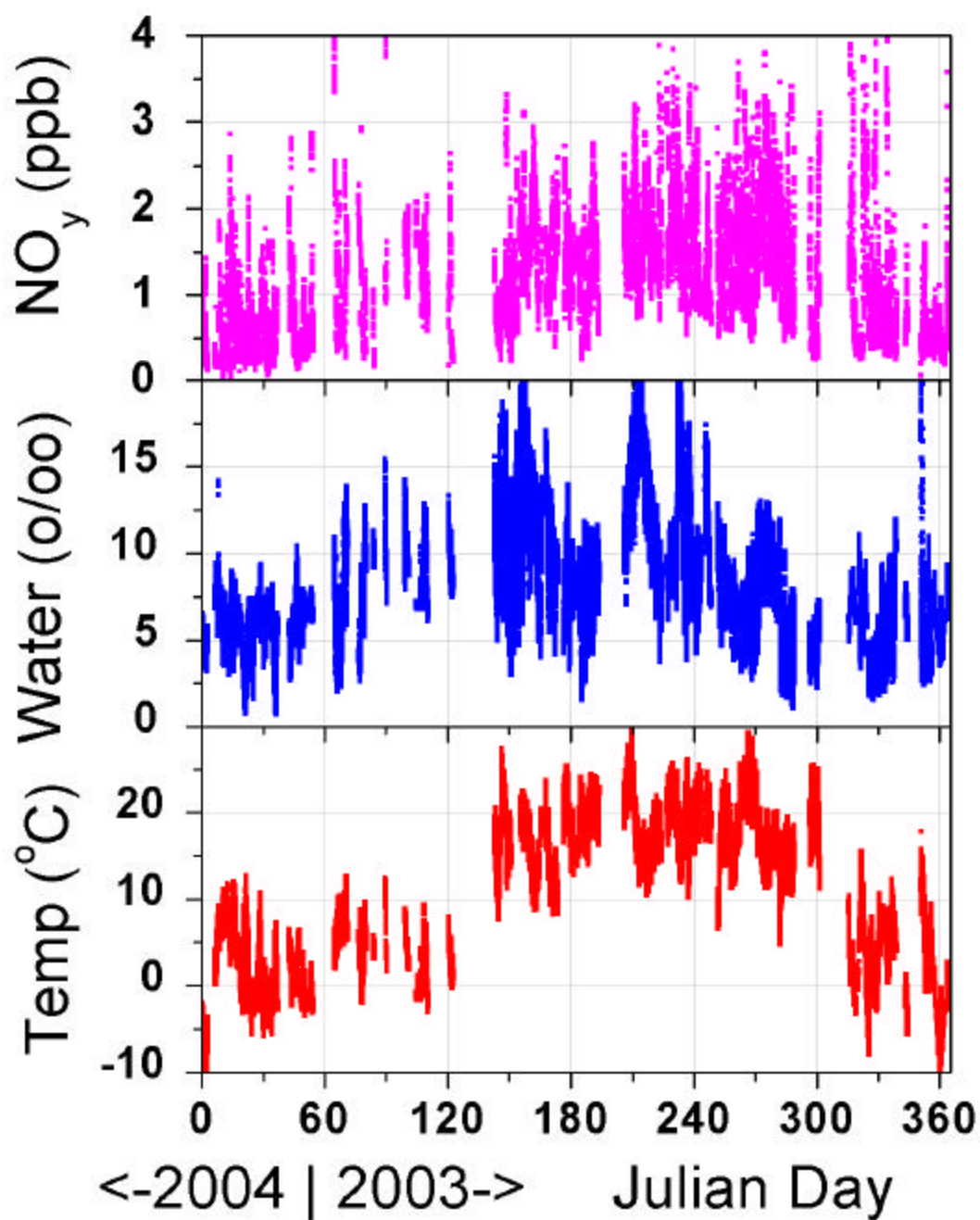
Figure 10. Full dataset obtained at the Big Hill monitoring site for NO_y, absolute water in parts per thousand, and temperature. Data acquisition began March 5, 2003 (day 64) and ended on Feb 23, 2004 (day 54).
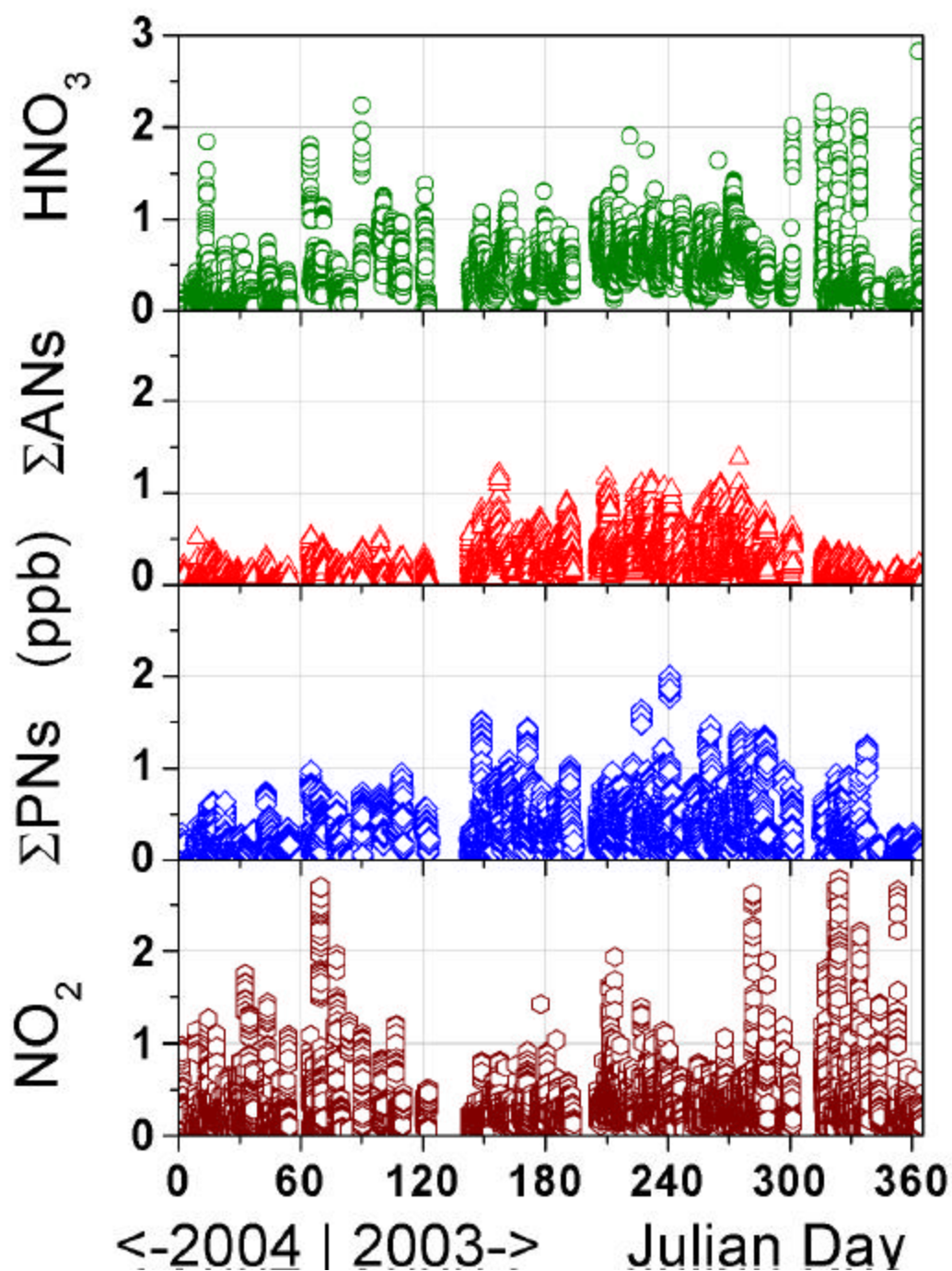
Figure 11. Annual record of individual NO_{yi} species, NO_2, ΣPNs, ΣANs and HNO_3 measured at Big Hill. Data points represent a 3-minute average and all concentrations are reported in parts per billion by volume.
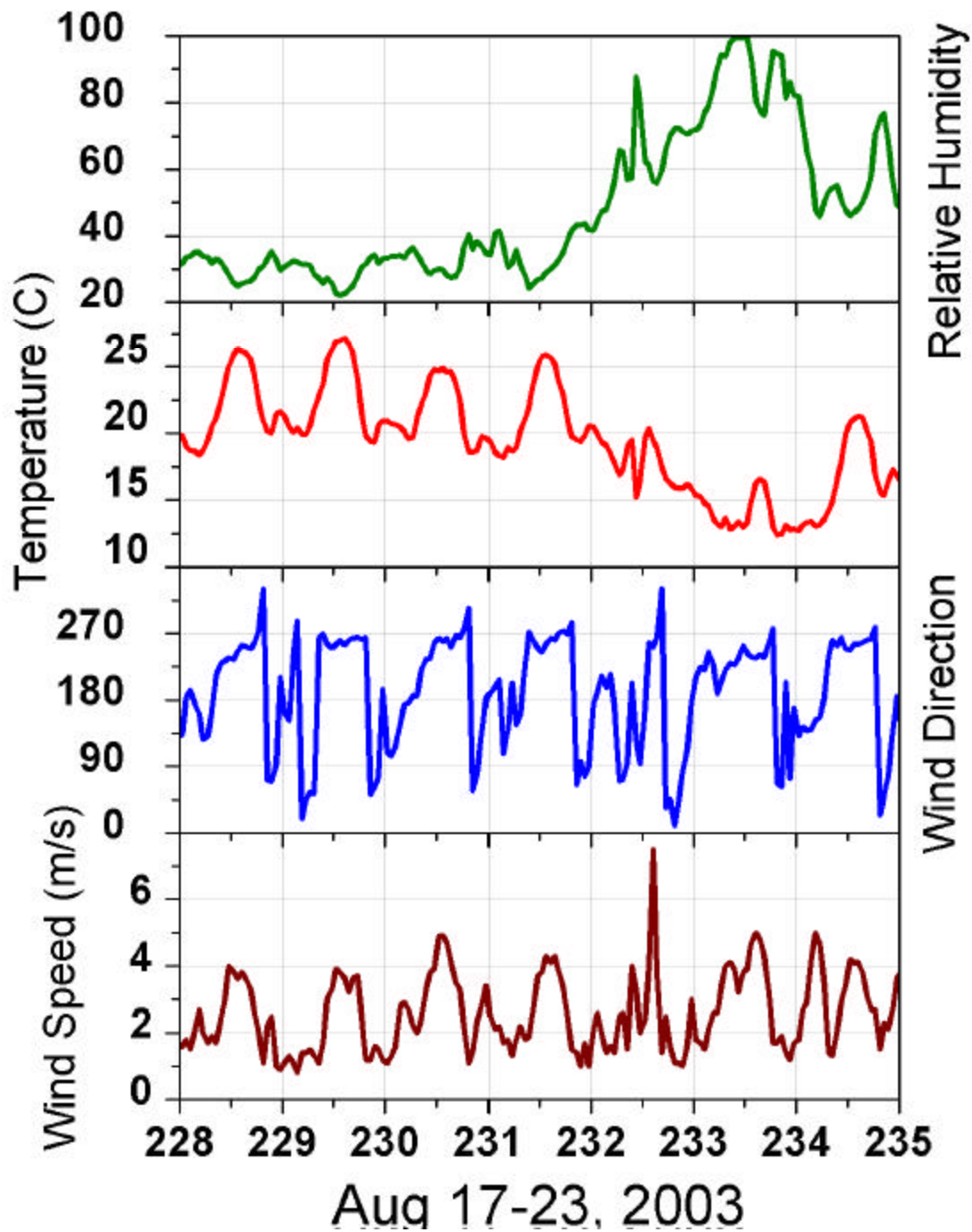
Figure 12. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) from a typical summer week at Big Hill.

Figure 13. Observations of NO_y and O_3 (ppb) and PM10 ($\mu g/m^3$) from a typical summer week at Big Hill.

Figure 14. Observations of NO$_2$, ΣPNs, ΣANs and HNO$_3$ from a typical summer week at Big Hill.

Figure 15. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) from a typical winter week at Big Hill.

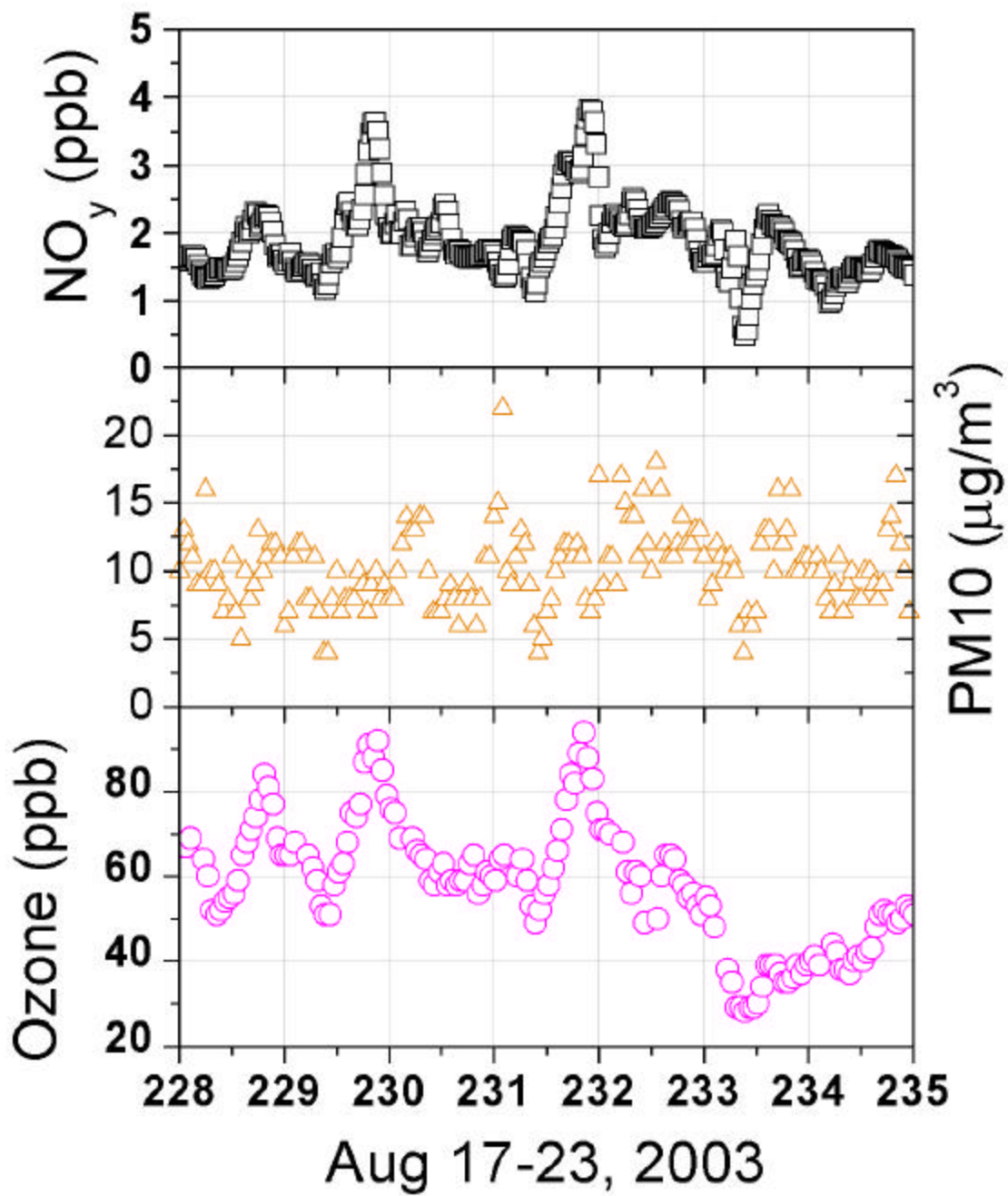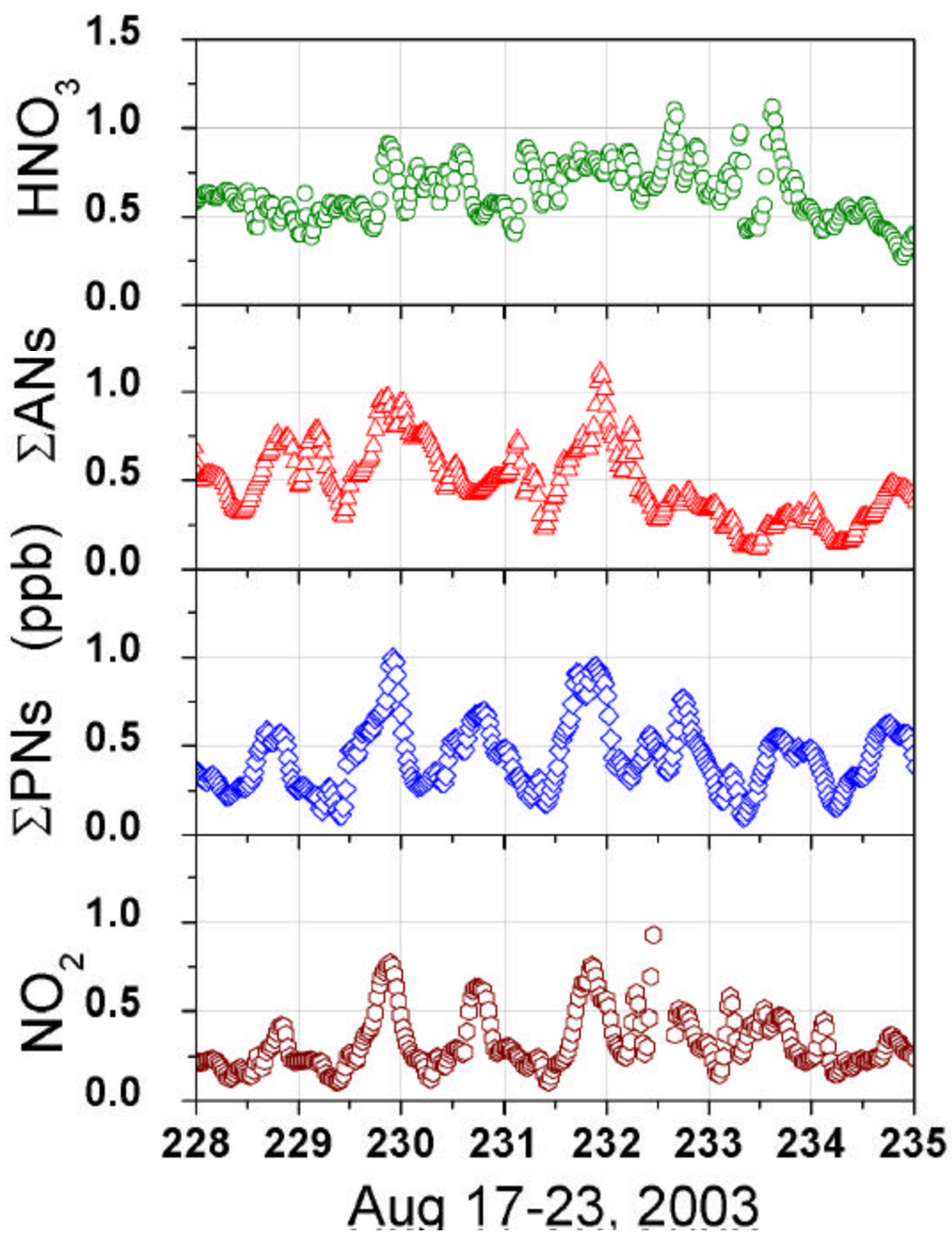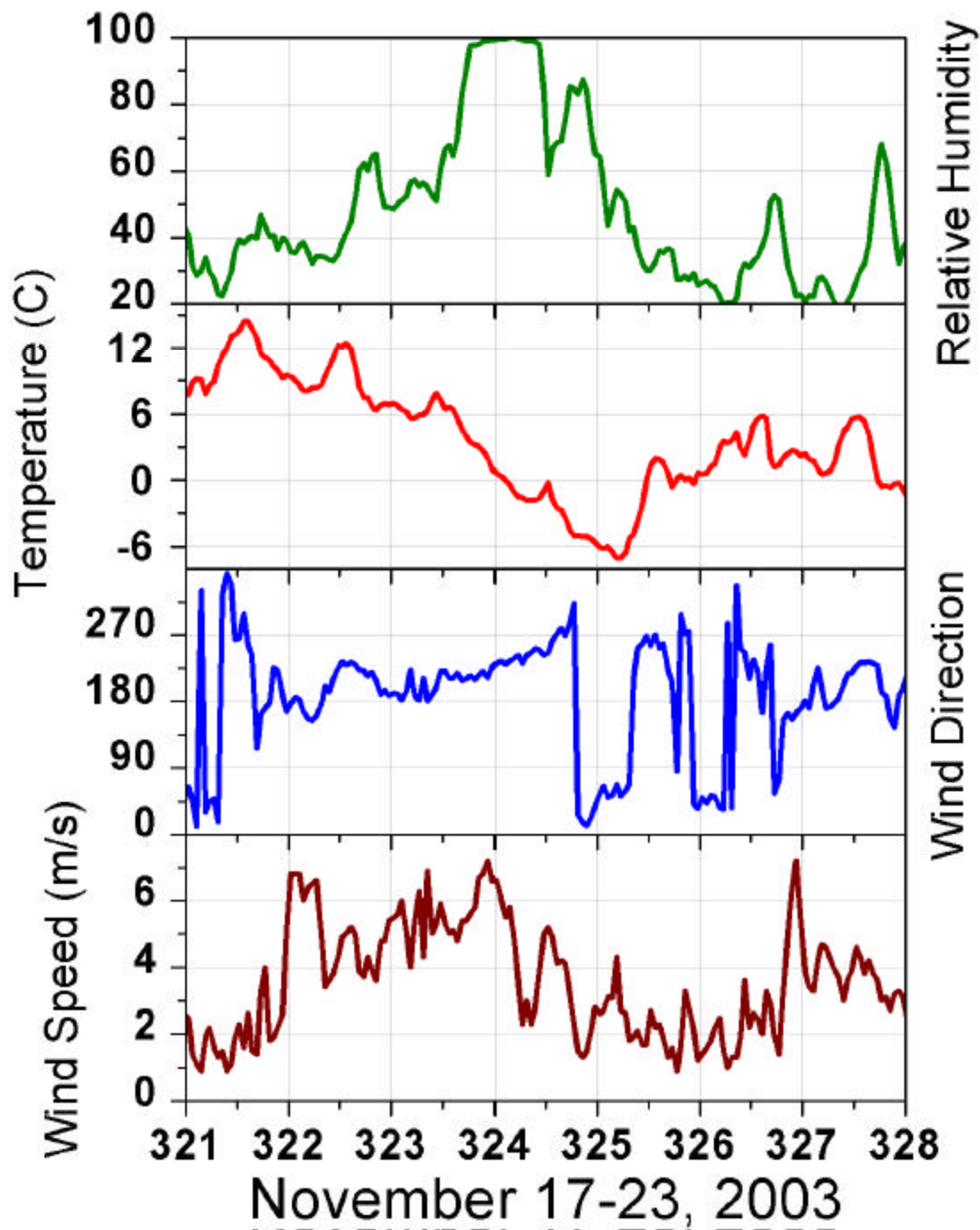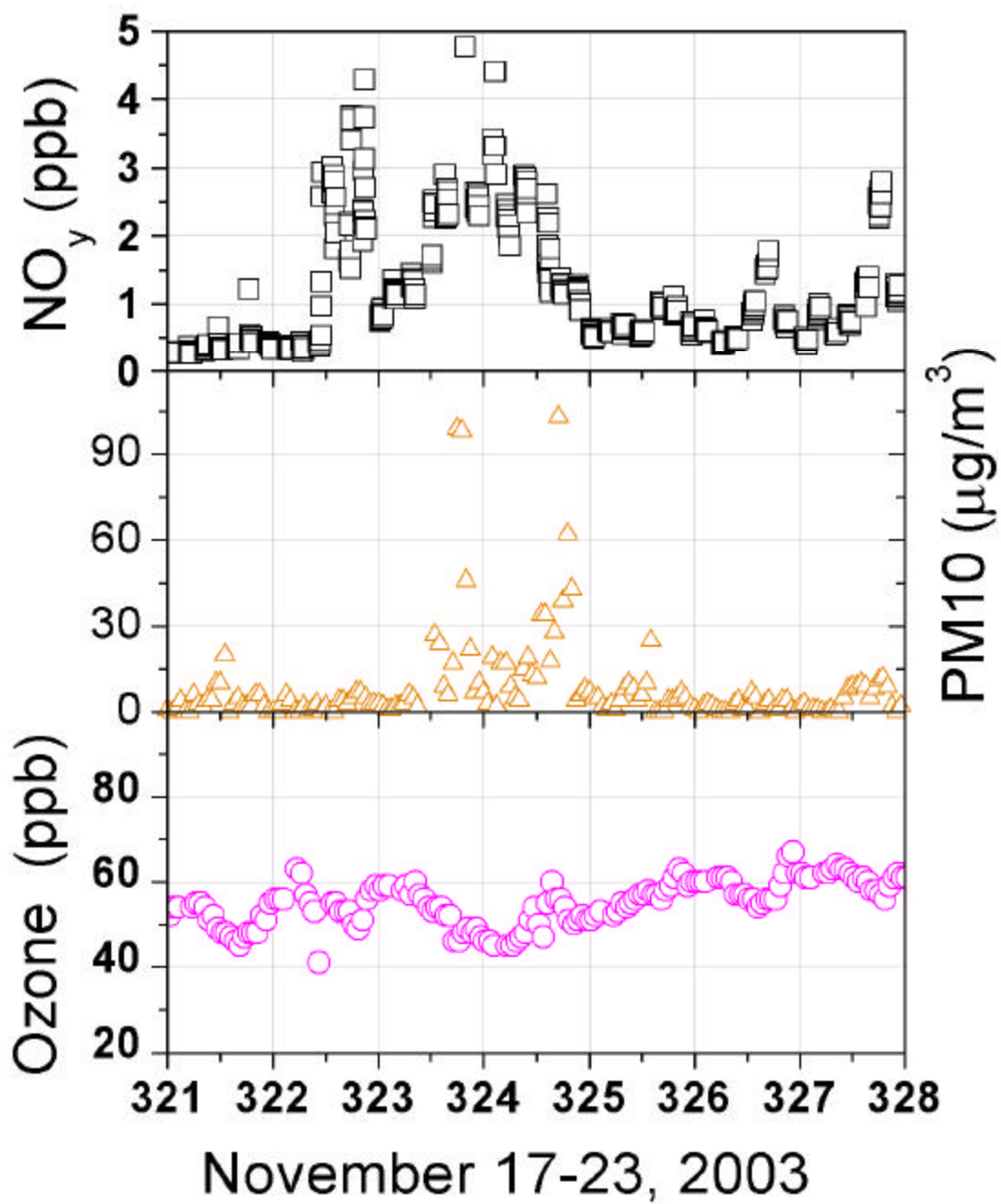Figure 16. Observations of NO_y and O_3 (ppb) and PM10 ($\mu g/m^3$) from a typical winter week at Big Hill.
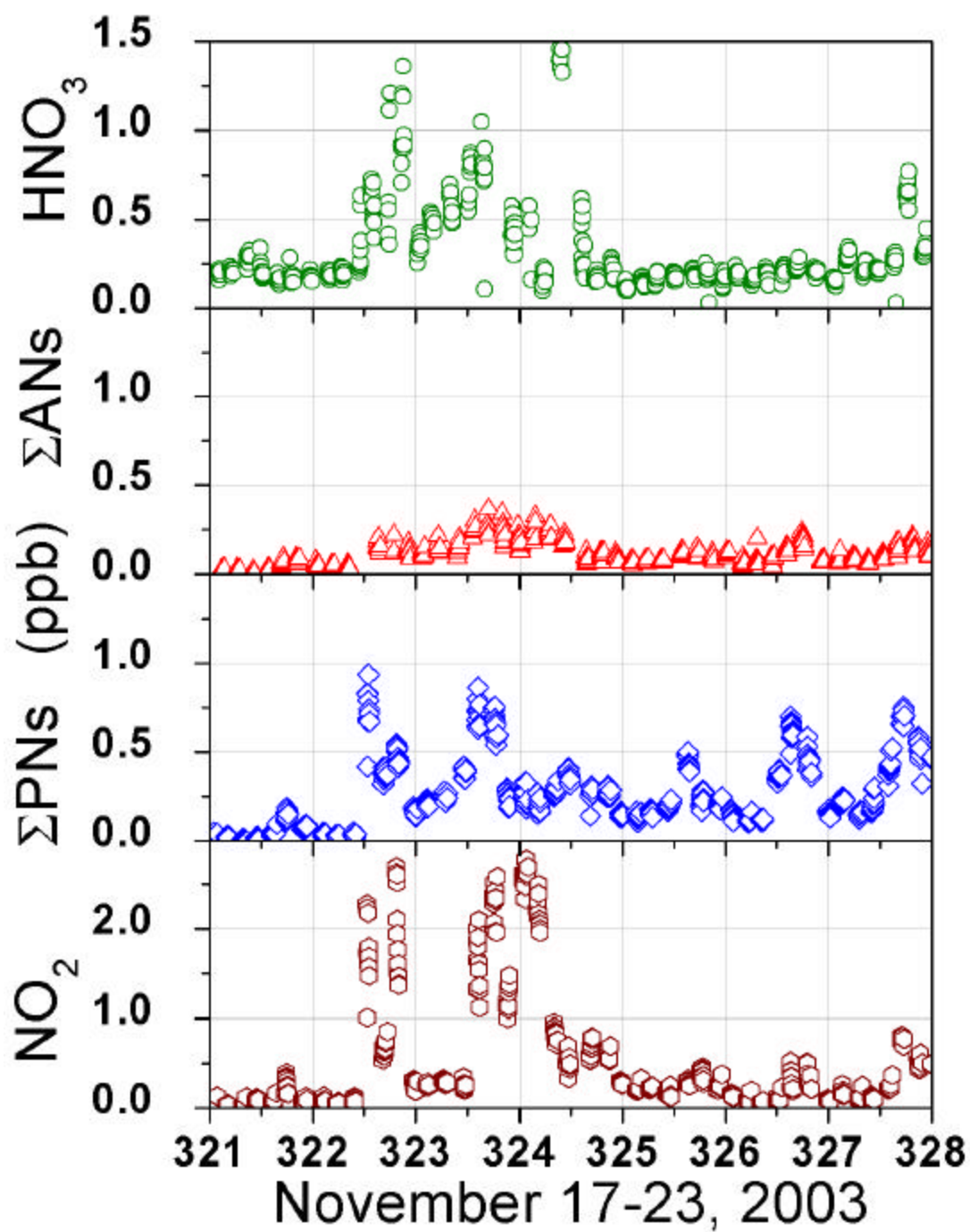
Figure 17. Observations of NO_2, ΣPNs, ΣANs and HNO_3 from a typical winter week at Big Hill. Note different axes on NO_2 panel.
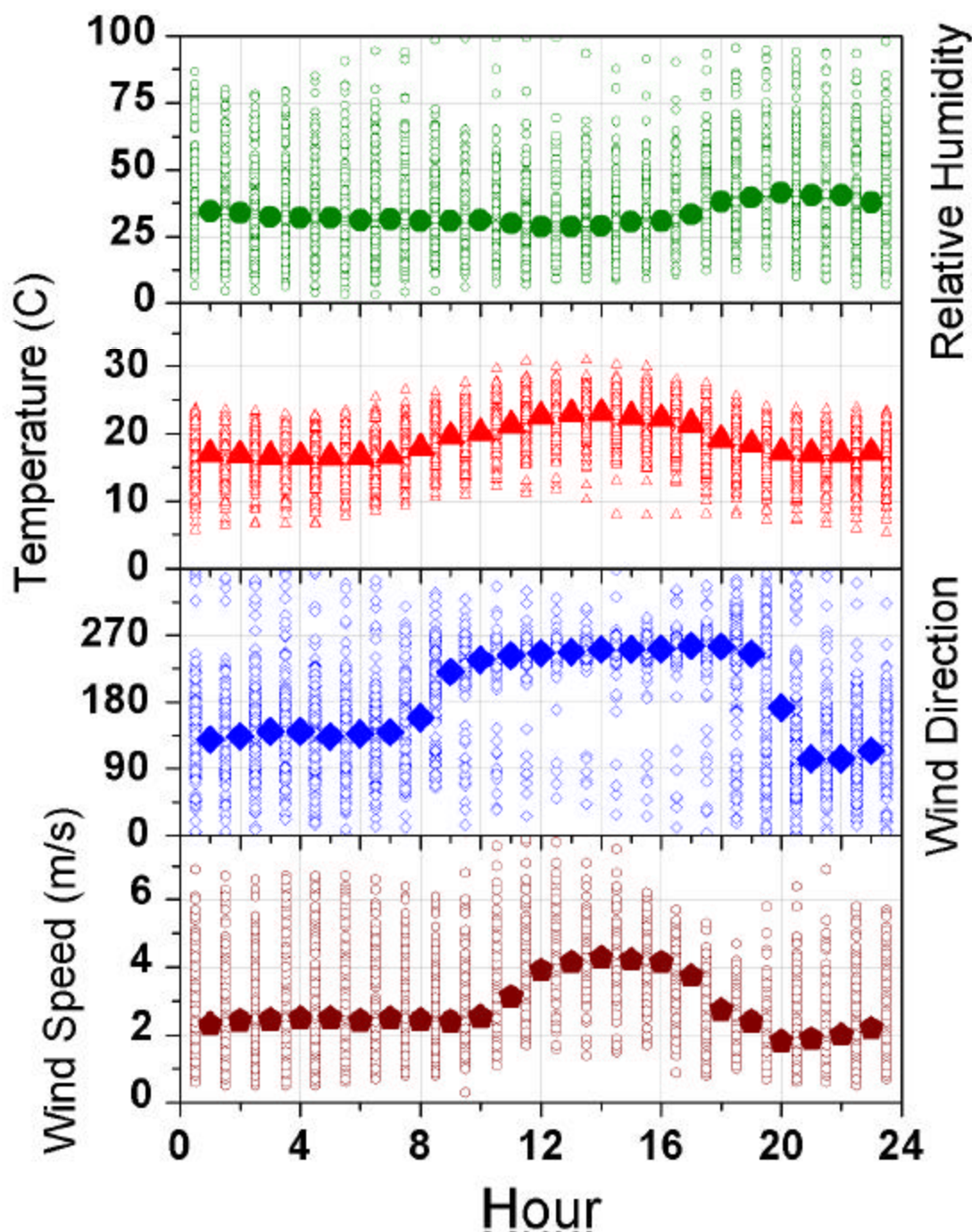
Figure 18. Observations of relative humidity (%), temperature (°C), wind direction, and wind speed (m/s) by hour of day for the entire summer (June through October) at Big Hill. Individual half hour data points for each day (open symbols) are overlaid by the averages for each half hour (solid symbols).
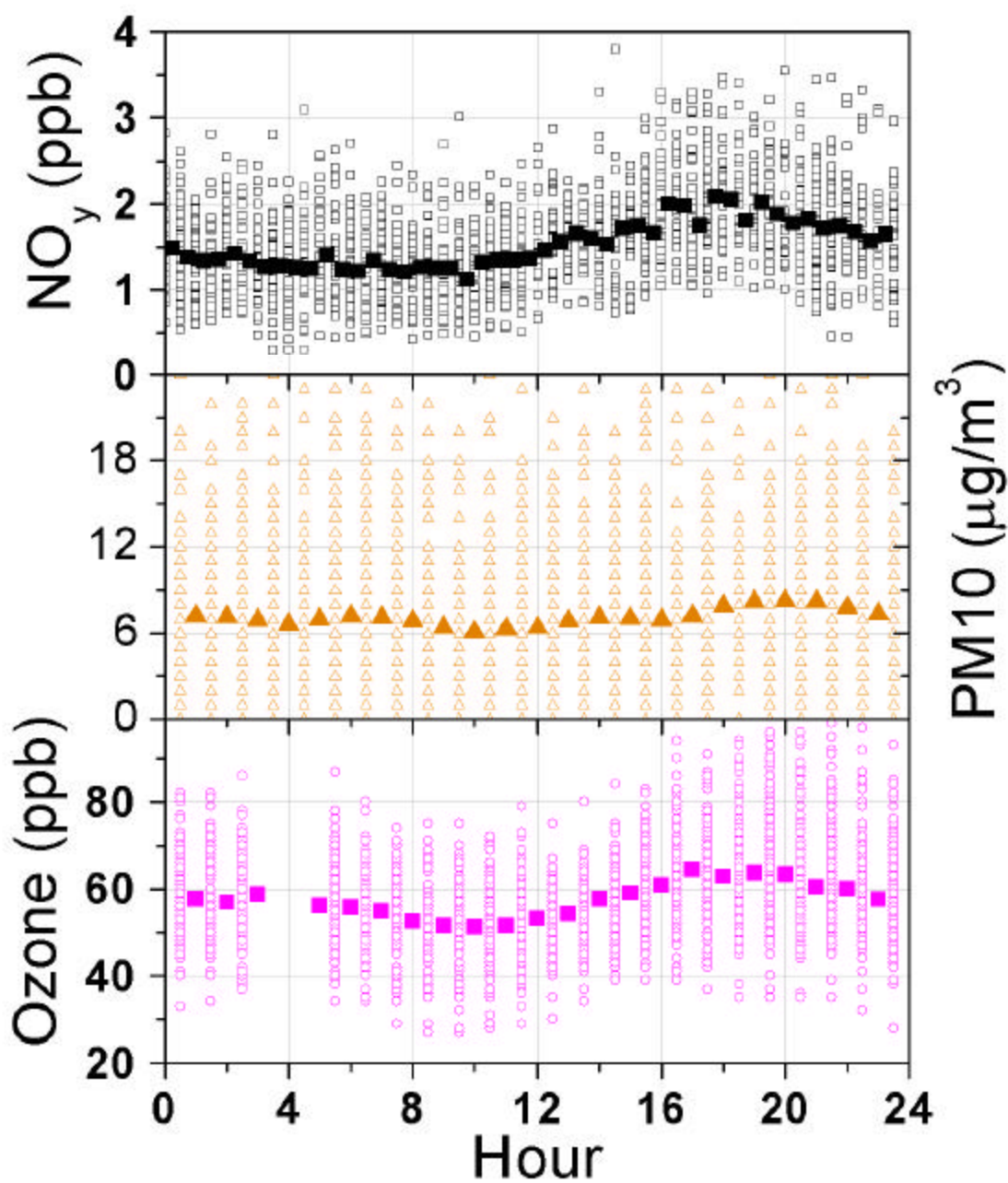
Figure 19. Diurnal profile of summertime observations of NO_y and O_3 (ppb) and PM10 ($\mu g/m^3$) at Big Hill. Individual measurements (open shapes) of O_3 and PM10 were made every hour at Big Hill, and the NO_y data has been averaged to half hour points. The average value for every hour or half hour is overlaid in the solid points.
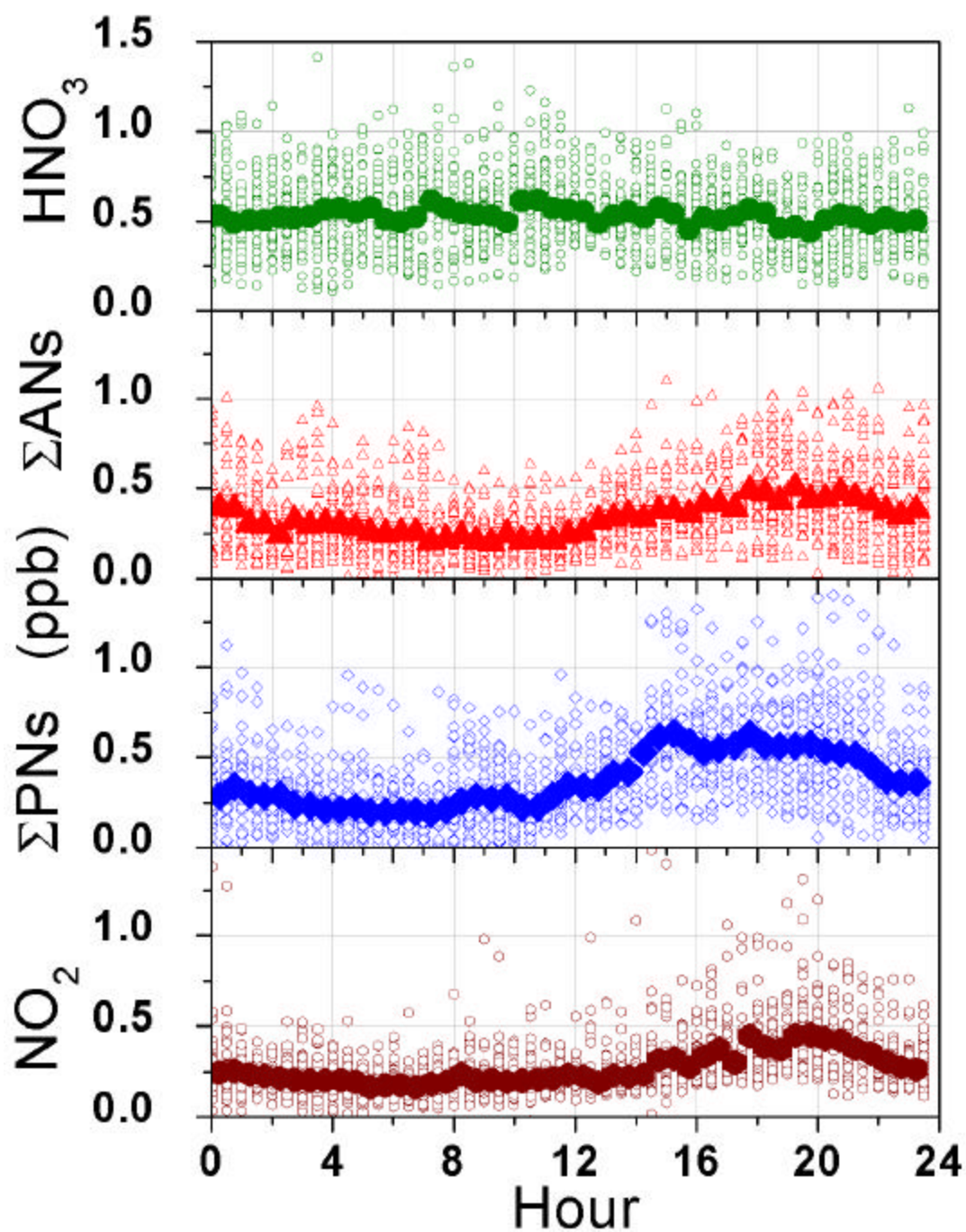
Figure 20. Diurnal profile of summertime observations of NO_2, ΣPNs, ΣANs and HNO_3 at Big Hill. Individual half hour data points for each day (open symbols) are overlaid by the averages for each half hour (solid symbols).
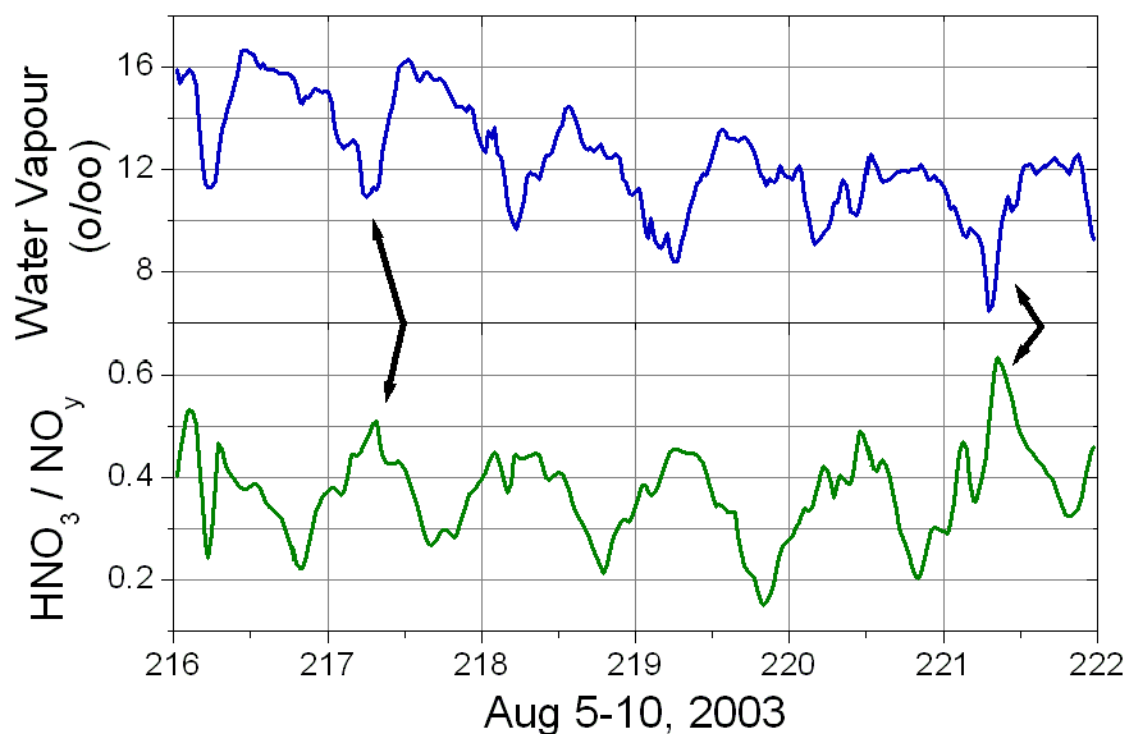
Figure 21. Time series of absolute water vapour (upper panel) and the fraction of total reactive nitrogen that is nitric acid (lower panel). Shortly after midnight on most days, the rapid drop in absolute water and increase in HNO_3/ NO_y suggest that air is mixing down from above which is drier and has not recently come into contact with the surface, therefore HNO_3 has not had the opportunity to deposit. The time series are generally anti-correlated, and arrows indicate two periods when sharp decreases in water are associated with an increasing importance of nitric acid in the reactive nitrogen budget.
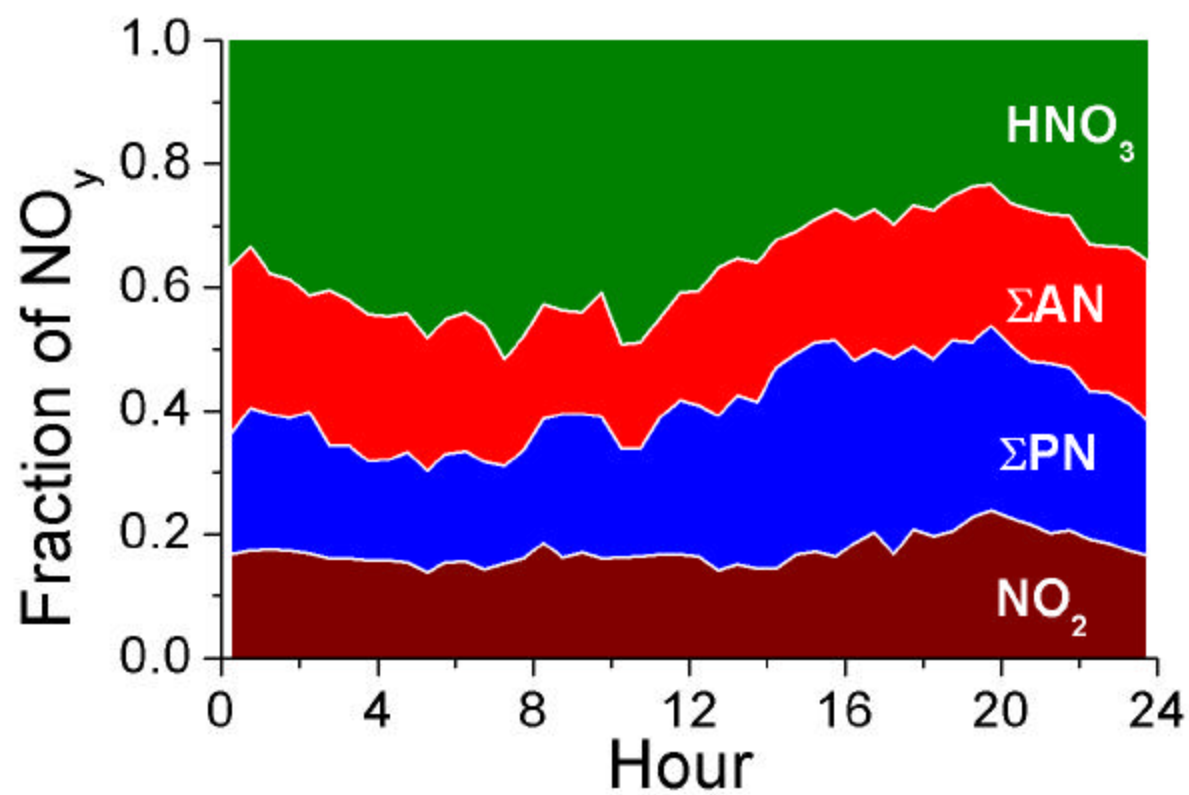
Figure 22. Fractional NO_y speciation by time of day during summer months at Big Hill.

Figure 23a
$T_{max} > 21°C$
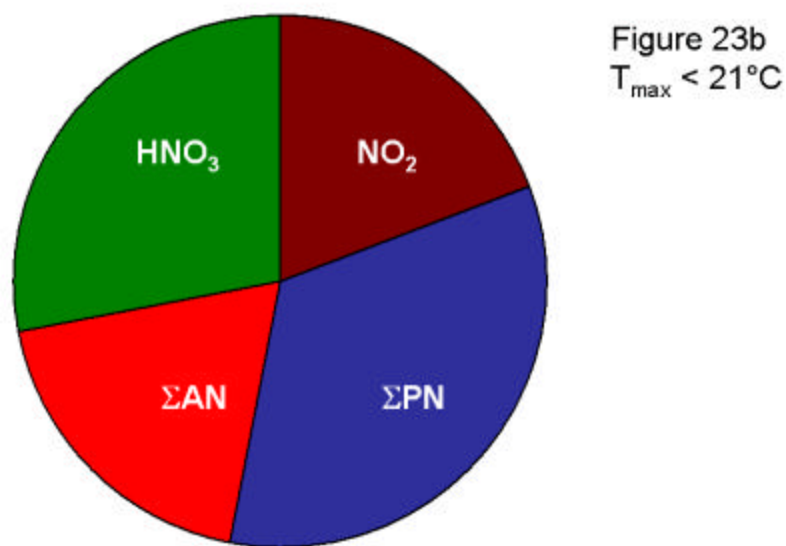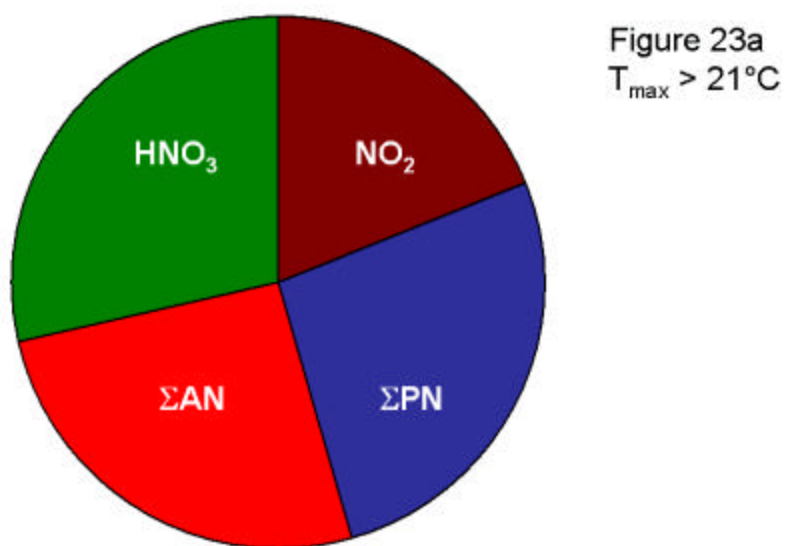
Figure 23b
$T_{max} < 21°C$

Figure 23. Distribution of NO_y during daytime upslope flow at Big Hill. The data was separated by temperature such that the top chart includes data from days on which the daytime maximum temperature at the site exceeds 20 °C, while the bottom chart shows data from cooler days on which the temperature was never higher than 20 °C.
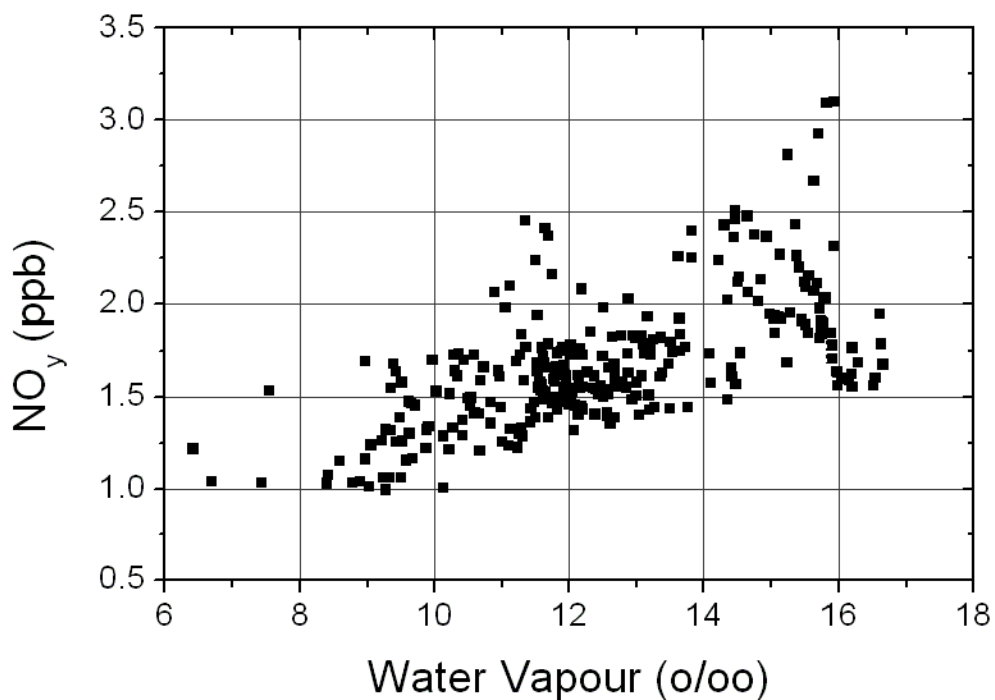
Figure 24. Relationship between reactive nitrogen (ppb) and mole fraction water vapour (parts per thousand) between Aug 5-10, 2003 at Big Hill.
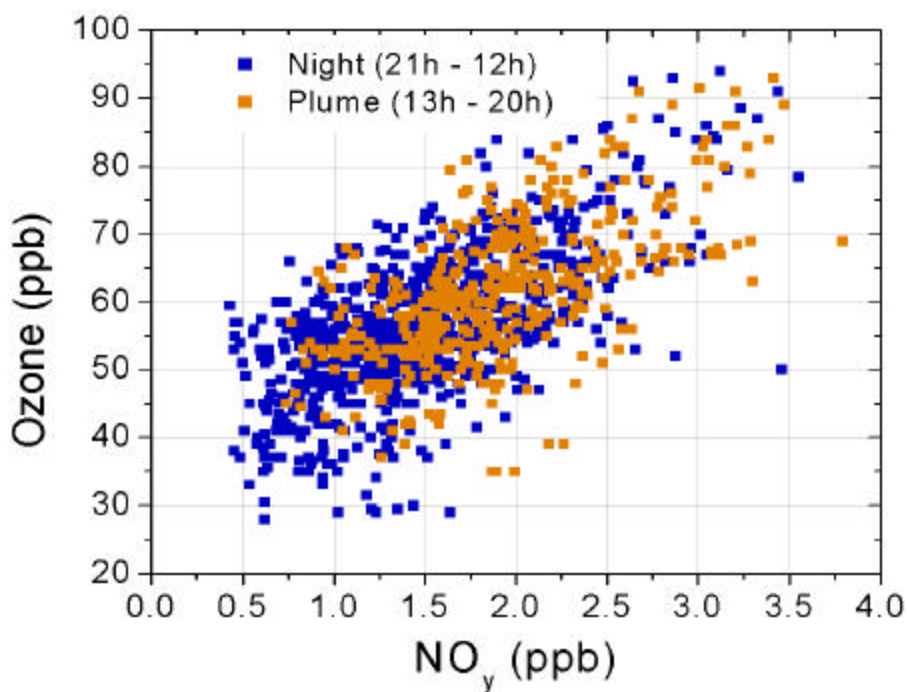
Figure 25. Relationship between ozone (ppb) and reactive nitrogen (ppb) during summer months at Big Hill. Observations made during upslope flow in the plume are in orange.
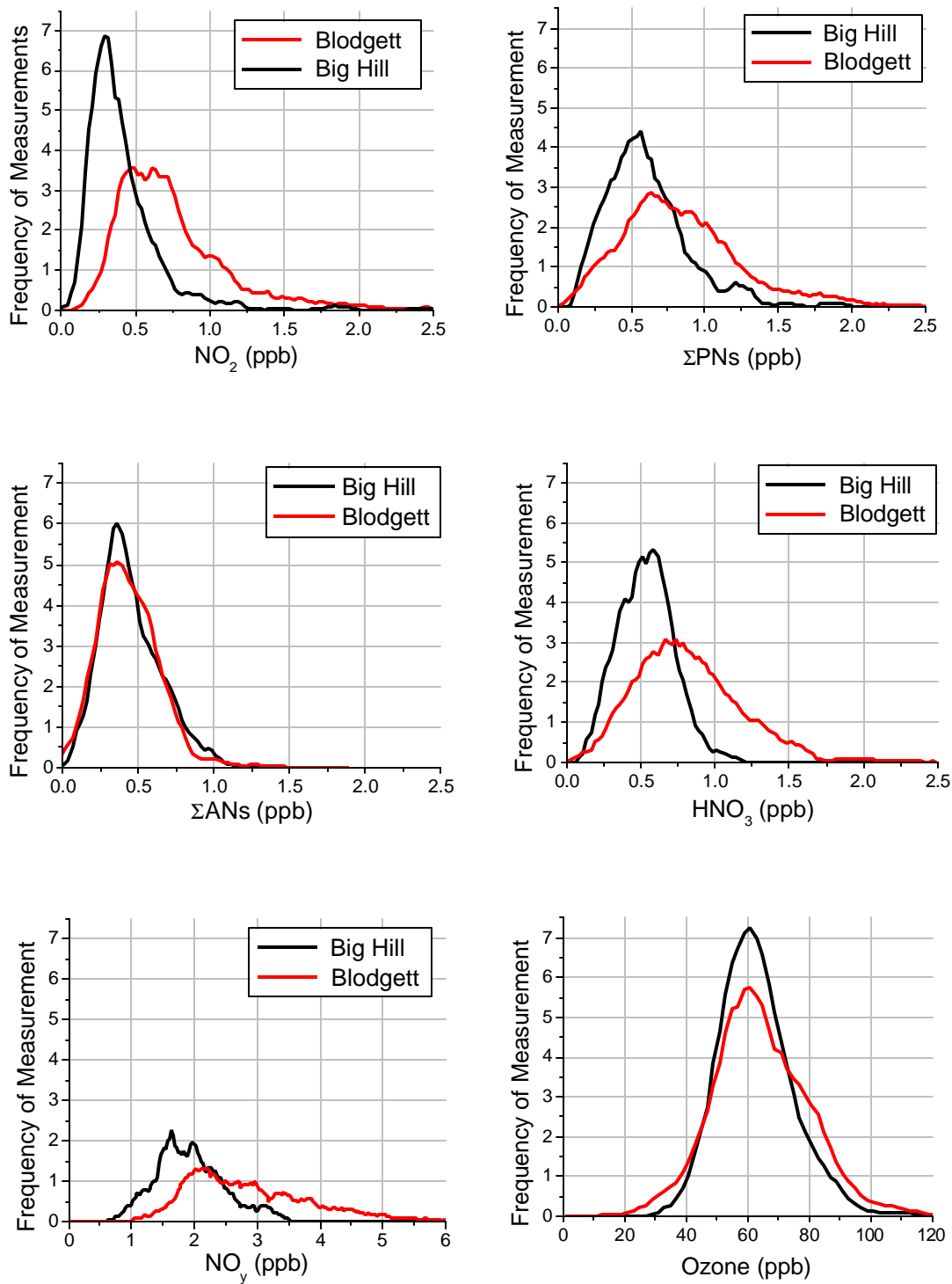
Figures 26a-f. Overlaid normalized probability distributions for half hour averages NO_{yi} and O_3 observations made during summer plume at Blodgett (red) and Big Hill (black)
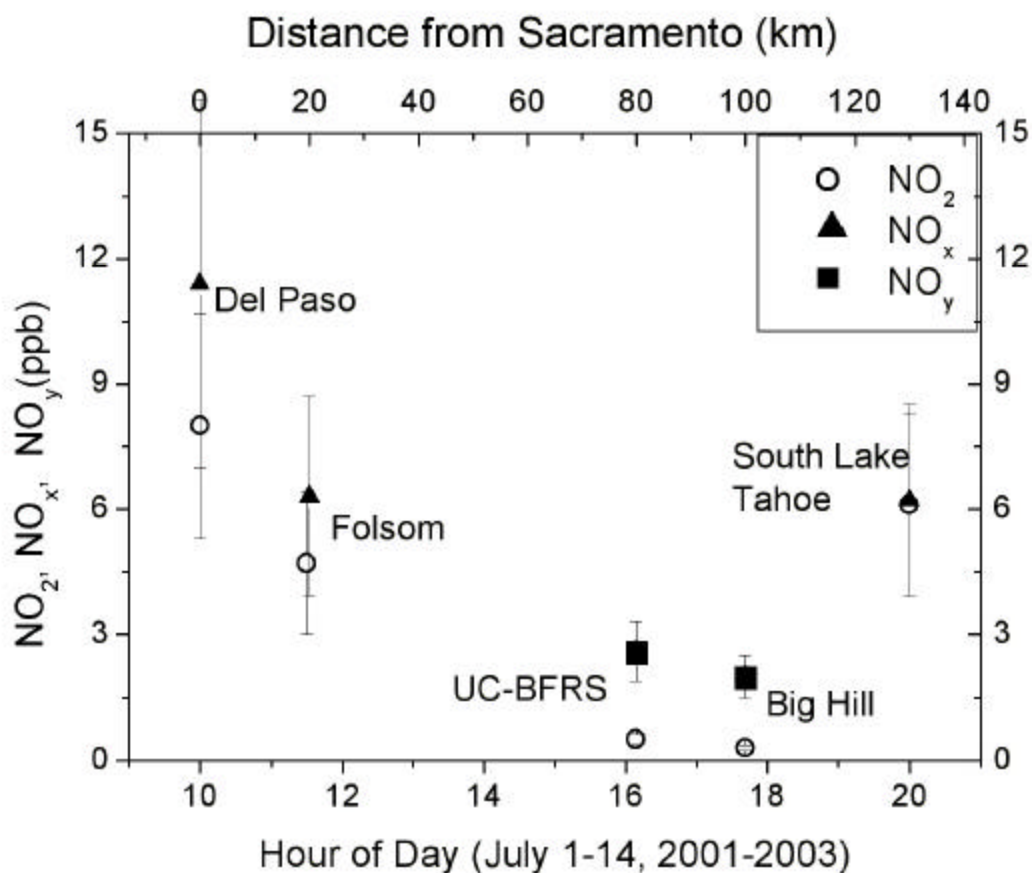
Figure 27. Reactive nitrogen observations along the Sacramento-Tahoe transect. The distance from Sacramento was multiplied by an average wind speed of 3.5 m/s to estimate the time the airmass would arrive at each site after leaving Del Paso at 10 am. Observations at each site were averaged for an hour around the estimated time. For example, UC-BFRS lies 80 km downwind of Del Paso, and NO_2 and NO_y observations between 3 pm and 5 pm were averaged to produce the points reported at 4 pm. The error bars represent the standard deviation of the average.

APPENDIX - **Chemistry and Transport of Nitrogen Oxides on the Western Slopes of the Sierra Nevada Mountains: Implications for Lake Tahoe**

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I. Introduction

Over the last 35 years, visibility into the depths of Lake Tahoe has decreased from 30 to 20 meters. Research suggests that a large part of this decline in water clarity is associated with increases both in fine sediment particles and in nutrient availability to microorganisms within the lake [*Jassby et al.*, 1999]. Estimates suggest that the productivity of microorganisms in the Lake was nitrogen limited in the late 1960s and 1970s, but that it is now primarily phosphorous limited [*Goldman et al.*, 1993]. Atmospheric deposition of phosphorus and nitrogen is thought to be an important mechanism for nutrient input to the lake, and direct deposition to the Lake has been estimated to account for about 50% of the combined annual input of these nutrients [*Jassby et al.*, 1994]. Additionally, atmospheric deposition to surfaces within the Lake Tahoe basin may substantially contribute to runoff into the Lake. In this review, we describe current knowledge of the concentrations of nitrogen oxides and their transport along the western slopes of the Sierra Nevada. We estimate the potential for precursors of particulate nitrates and nitric acid emitted in the Central Valley to reach the Lake Tahoe Air Basin. We also comment on transport of non-reactive nitrogen species such as ammonia.

Most deposition of bioavailable nitrogen from the atmosphere occurs in the form of nitric acid (HNO_3), ammonia (NH_3), ammonium (NH_4^+), or nitrate (NO_3^-). However, many additional nitrogen-containing chemicals are found in the atmosphere and most of them are removed by deposition, although more slowly than HNO_3. Sources of atmospheric nitrogen in the Lake Tahoe Air Basin include in-basin sources, including those associated with stationary and mobile combustion, with fertilizer application, and with redeposition of biogenic emissions from the local ecosystems. A similar mixture of sources contribute to nitrogen transported from outside the basin: there is a global background of concentrations of nitrogen oxides and NH_3/NH_4^+ that

sets a lower limit on the bioavailable nitrogen; emissions from urban and farming centers to the west of the Lake add to this background; mobile sources that travel between those centers and the Tahoe basin are also a significant source of emissions; and finally natural emissions from the ecosystems located between the Central Valley and Lake Tahoe are also sources of nitrogen-containing compounds.

While several studies have addressed the potential transport of pollutants from the Central Valley to more remote locations, many of them focus on individual events and, especially in the case of ozone studies, extreme events that lead to air quality violations. In relation to nitrogen deposition, the cumulative effects of transport on seasonal and annual timescales need to be considered. Short term studies can be used to identify possible transport patterns or occurrences but long term observations are required for an accurate representation of the overall contribution of transport to the deposition of N within the Tahoe Basin. Sections II and III of this report deal with dry deposition of reactive nitrogen, which refers to the direct transfer of gas and particle phase species to the Earth's surface without the aid of precipitation. Section IV examines the role of wet deposition, in which airborne species are transferred to the surface in aqueous form, such as rain, snow or fog. Estimates in Jassby at al [*Jassby et al.*, 1994] and Tarnay et al [*Tarnay et al.*, 2001] suggest that wet deposition contributes one half to two thirds of direct atmospheric N deposition to the surface of Lake Tahoe.

II. Chemistry of Nitrogen Oxides

Nitric oxide (NO) is the primary reactive nitrogen compound emitted by biological activity and as a byproduct of combustion. Once emitted, NO rapidly (~100 seconds) interconverts with NO_2

$$NO + O_3 \rightarrow NO_2 \qquad\qquad R_1$$

$$NO_2 + light + O_2 \rightarrow NO + O_3 \qquad\qquad R_2$$
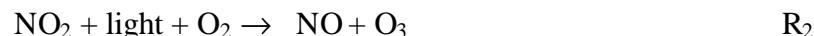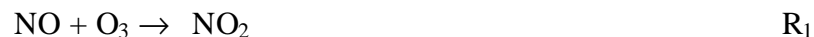
Collectively, NO and NO_2 are referred to as NO_x and the sum of NO_x and all higher oxides of nitrogen is referred to as NO_y. Higher oxides of nitrogen are formed in reactions of the radicals OH, HO_2 and RO_2 with NO and NO_2, principally:

$$NO_2 + OH \rightarrow HNO_3 \qquad\qquad R_3$$

$$NO_2 + R'(O)O_2 \rightarrow R(O)O_2NO_2 \qquad\qquad R_4$$

$$NO + R''O_2 \rightarrow RONO_2 \qquad\qquad R_5$$
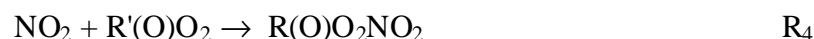
These reaction products have very different properties. Peroxynitrates are thermally unstable and form a reservoir for NO_x, in which the partitioning depends on the ambient temperature. HNO_3 and hydroxyalkyl nitrates (R'' = ROH) are very water soluble while the peroxy nitrate and alkyl nitrate products of R_4 and R_5 are only weakly water soluble. As a result of its solubility, HNO_3 is rapidly (on a time scale of hours within the planetary boundary layer) removed from the atmosphere by deposition to the Earth's surface and/or rapidly scavenged in water-rich aerosols, which then deposit to the Earth's surface. Less is known about the deposition rates of hydroxyalkyl nitrates but measurements of their Henry's law solubilities strongly suggest that their deposition rates should be similarly to that of HNO_3. Deposition of NO_2, alkyl nitrates, and peroxynitrates are a factor of 10 slower than deposition of HNO_3 [*Wesely and Hicks*, 2000]. The most abundant peroxynitrate, PAN, is a known phytotoxin at the concentrations (~5 ppb) encountered immediately downwind of Sacramento [*Cape*, 2003]. HNO_3 also reacts with NH_3 in the gas phase or within particles to produce an ammonium nitrate salt: NH_4NO_3. The equilibrium is shifted toward ammonium nitrate aerosol at low temperature and high relative humidity, and the particles may have different atmospheric lifetimes than gas phase HNO_3 [*Seinfeld and Pandis*, 1998].

$$NH_3(g) + HNO_3(g) \rightarrow NH_4NO_3 (s) \qquad\qquad R_6$$
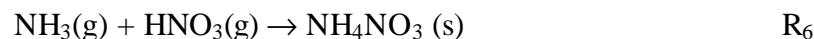
The nitrate radical, NO_3, is formed from the oxidation of NO_2 by O_3 (R_7). However, NO_3 is rapidly destroyed by sunlight (R8).

$$NO_2 + O_3 \rightarrow NO_3 \qquad\qquad R_7$$

$$NO_3 + light + O_2 \rightarrow NO_2 + O_3 \qquad\qquad R_8$$
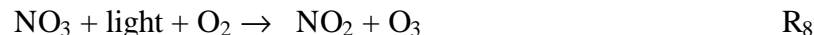
At night, when the very rapid photolysis of NO_3 (R_8) is not occurring, NO_3 accumulates and then reacts to form N_2O_5 via R_9:

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad\qquad R_9$$

HONO is also rapidly photolyzed during the day and accumulates at night as a result of mechanisms that are poorly understood, but appear to be equivalent to:

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \qquad\qquad R_{10}$$

N_2O_5 and HONO are highly reactive with and soluble in water and are likely removed from the atmosphere on contact with most surfaces. The role of these important nighttime compounds in redistributing reactive nitrogen is not well understood.

III. Transport

Transport of nitrogen oxides from the Central Valley and the western slopes of the Sierra Nevada to Lake Tahoe can result from processes including: a) direct transport within the planetary boundary layer (PBL), b) direct transport above the PBL, c) accumulation of pollutants in a regional background, and d) incorporation of nitrogen oxides into cloudwater (Figure 1). The first two of these mechanisms operate on a timescale of several (5-20 hours). Accumulation of pollutants in a regional background and subsequent transport to Tahoe operates on longer timescales (multi-day). The first three of these mechanisms are expected to operate, though to differing extents, every day, while the last mechanism depends on the presence of clouds. Research also suggests that biomass burning may be a significant source of atmospheric nitrogen and phosphorus in the Lake Tahoe Basin [*Zhang et al.*, 2002] and it is well known that biomass fires can be significant sources of longer lived pollutants such as CO on a continental scale [*Novelli et al.*, 2003]. Fires are episodic in nature, the extent to which their emissions will impact the Basin rests on their frequency, intensity, and proximity to Tahoe.

The overall impact of remote sources of atmospheric reactive nitrogen on Lake Tahoe depends on the appropriately weighted combination of all of the above pathways. The prevailing circulation at this latitude is westerly, and at altitudes more than 2000 m, surface topographical features should not disturb this large scale flow pattern. Near the surface in the summertime, marine air penetrates the Carquinez Strait, moves through the delta region and splits north and south to flow through the Central Valley [*Schultz et al.*, 1961; *Frenzel*, 1962; *Hays et al.*, 1984]. Superimposed on this dominant flow pattern, daytime heating of the western Sierra Nevada generates upslope winds that transport air from the valley floor into the mountains, regardless of the dominant flow regime within the Central Valley itself [*Zaremba and Carroll*, 1999]. In winter, significant periods of high pressure in the region cause inland valleys and basins to fill with cold air leading to low mixing heights and weak winds. Local pollutants tend to accumulate and long range transport of emissions is less likely. While the pattern of upslope/downslope flow is observed on some winter days, the shorter periods of daylight mean that upslope flow persists for a much smaller fraction of the day: the extent to which airmasses travel along Arrow 4 in Figure 1 is greatly reduced. Figure 2 shows the summer and winter patterns of upslope/downslope flow at the University of California's Blodgett Forest Research Station (UC-BFRS, 1400 m ASL).

Figure 1 depicts the transport pathways of pollutants originating in the Central Valley and being advected toward the Tahoe Basin. The dotted line is used to suggest the mixing height or upper edge of the planetary boundary layer. Analysis of observations from a network of radar wind profilers and radio acoustic sounding systems confirm that wind patterns observed at the surface extend to 800-1000 m above the surface [*Zhong et al.*, 2004]. Urban emissions may be transported within the PBL along path 1 or lofted above and transported in the free troposphere by path 2,3. If westerly flow is strong enough or persists long enough during a given day, it may reach the Tahoe Basin. Arrow 4 is dotted to emphasize that it is unclear how often conditions directly transport an air parcel originating in the valley this far east before the winds turn around at night. While pollutants may not be directly transported to Tahoe within the surface layer, emissions into an air mass that sloshes up and down the slope of the Sierra every day will increase the regional background over time, contributing to elevated regional reactive nitrogen in air that may reach the Tahoe Basin. A detailed understanding of how air within the Tahoe Basin mixes (arrow 5) is also necessary to assess the influence of remote nitrogen sources. Pollutants

transported aloft via pathway 2,3 will have no effect on Lake Tahoe unless they enter the mixed layer above the lake, which would permit their eventual deposition. An assessment of the probability of such events is beyond the scope of this review. It is evident from Figure 1 that atmospheric measurements made at surface sites along the Sacramento-Tahoe transect do not give us information about the mechanisms involved in wet deposition in the Lake Tahoe Basin. Supplementary references were used to estimate the relative contributions of global, regional and in-basin sources of reactive nitrogen to wet deposition in Section IV.

IIIa. The urban plume

The daily evolution of the Sacramento urban plume during the summer is remarkably consistent. During the day, terrain driven winds blow steadily from Sacramento into the Sierra Nevada foothills – drawing air into the sparsely populated mountains. During the night, the wind reverses and clears out the mountains replacing the urban plume with the regional background. Observations of atmospheric composition and meteorology show this pattern persists up to at least 1200 m elevation along the Sierra slopes [*Carroll and Dixon*, 2000]. Transport of anthropogenic emissions from the Sacramento metropolitan area as a result of this meteorological flow pattern is evident in observations of anthropogenic hydrocarbon, ozone, and nitrogen oxide concentrations at the University of California Blodgett Forest Research Station, which peak in the late afternoon/evening and decrease steadily with the downslope flow during the night. *Van Ooy and Carroll* [1995] measured ozone and local meteorological variables (temperature, wind speed, wind direction, relative humidity, and solar radiation) at six sites along a 400 km north-south transect of the Sierra Nevada foothills (1100 – 1200 m elevation) during the summer of 1992. At the three sites where east-west wind patterns are predominant, as they also are at UC-BFRS, there was a strong correlation between wind direction and ozone concentrations. At these sites, there was a regular diurnal pattern with ozone concentrations peaking at 15:00 to 17:00 PST (Pacific Standard Time) and reaching a minimum at 7:00 PST. At the other three sites where north-south winds were predominant, the diurnal variation in ozone was small. The sites with east-west wind patterns had higher peak ozone abundances and violated the one hour state ozone standard of 90 ppb up to 40% more often than the sites with predominantly north-south winds indicating sites with east-west wind patterns such as UC-BFRS

represent a maximum effect of transport. The major climate variables controlling transport in the region (temperature, sunlight, precipitation, relative humidity, and wind) as measured in Sacramento have been nearly constant for 20 years (1980 to 1999) (Figure 3). Thus emissions in the Central Valley should have been transported with equal efficiency throughout this 20-year period.

These analyses suggest the plume travelling into the foothills of the Sierra from the Valley serves as a mesoscale (~100 km) daytime flow reactor that can be characterized as a Lagrangian air parcel transported from the Valley into the Sierra Nevada. *Dillon et al.* [*Dillon*, 2002; *Dillon et al.*, 2002] used comprehensive (ozone, speciated nitrogen oxides, speciated anthropogenic and biogenic hydrocarbons, and meteorology) and extensive observations (spanning the years 1997 to 2002) at Folsom, California and five hours downwind at the UC – Blodgett Forest Research Station to evaluate transport from Sacramento into the mid-Sierra during the summer (Figure 4). The observations at Folsom effectively integrate all of the emissions to the west. *Dillon et al.* (2002) established that a Lagrangian analysis captures the essential features of the chemistry and transport and fit the parameters of a Lagrangian model to the observations. Comparison of ozone and meteorological observations to the north of UC-BFRS at Blue Canyon and to the south at Sly Park support the suggestion that the observations and the model analysis are regionally representative *Dillon et al.* [*Dillon*, 2002; *Dillon et al.*, 2002].

Measurements of NO_y and individual NO_y species at UC-BFRS (1998-present) demonstrate pronounced seasonal variability [*Day et al.*, 2002] (Figure 5). The Lagrangian model has only been applied to summer time conditions when upslope transport is expected to be at a maximum. To obtain an annually complete picture, other approaches are required to interpret the reactive nitrogen measurements because of different source distributions, and more importantly, very different meteorological conditions.

Mixing

Parameters in the model described by *Dillon et al.* (2002) include mixing of the urban plume with the regional background, chemical processing, emission and deposition. Mixing of the plume (exchange between $[X]_S$ and $[X]_F$ in Figure 1) occurs on a time scale of 4 hours during daytime upslope flow. Treating NO_y as a conserved quantity in calculations represents an upper

limit to the contribution of urban NO_y in the Sierra Nevada since chemical factors also act to reduce NO_y. Based on mixing alone, by the time the plume arrives at UC-BFRS, 5 hours downwind from the suburbs of Sacramento, the urban emissions are diluted to 28% of their initial concentration by mixing with the background. If we extrapolate these results to Tahoe, which is another 4 hours downwind, the urban portion of the concentrations would be 10% of their initial values. In the summer, the regional background in the area is estimated to be 1.9 ppb, and daytime NO_y mixing ratios in the downwind suburbs of Sacramento are 7 ppb, thus 5.1 ppb is the direct result of local emissions. Based on mixing alone, after five hours of transit the concentration of NO_y at UC-BFRS would be 3.4 ppb (1.5 ppb from the plume, and 1.9 from the regional background). Extrapolating to Lake Tahoe, the concentration of NO_y would be 2.4 (0.5 ppb from the plume, and 1.9 from the regional background). Observations by *Carroll et al.* (2002) along a transect at 2000 m suggest the urban plume usually stops there (Arrow 4 does not extend above 2000 m) and does not progress across the pass into the Lake region, indicating that direct transport of inorganic nitrogen from the Central Valley is likely smaller than this estimate. This would suggest that depending on the dynamics, the upwind contribution of NO_y to the Tahoe Basin may be better described by $[X]_F$ rather than $[X]_S$. If air that has traveled along the surface reaches the Tahoe Basin, the concentrations of anthropogenic emissions will have been substantially reduced by mixing and deposition, and the direct influence of the urban plume will have been transformed into an elevated regional background due to the pattern of recycling flow.

HNO₃ formation and deposition

Chemical production of HNO_3 followed by rapid deposition removes NO_y reducing the urban contribution below the estimate given above for mixing alone. *Dillon et al.* (2002) determined that the effective OH mixing ratio that acts over the 5-hour transport time to Blodgett Forest is about 1.4×10^7 molecules/cm^3 or (0.6 ppt). NO_2 reacts rapidly with OH to form HNO_3 ($k\sim9\times10^{-12}$ s^{-1} cm^3/molec) and in the absence of other reactions of NO_2, approximately 90% of the suburban NO_2 would be converted to HNO_3 prior to reaching UC-BFRS. HNO_3 is deposited on a time scale set by the ratio of the deposition velocity to the boundary layer height. Using literature estimates for the deposition velocity (0.035 m/s) [*Hanson and Lindberg*, 1991] and the boundary layer height (800 m) [*Seaman et al.*, 1995], results in a lifetime of 6.3 hours. Thus, about 50% of the HNO_3 formed during the transit to UC-BFRS is deposited along the way and about 85% is deposited before it gets to the Tahoe basin. *Day et al.* [*Day et al.*, 2002] provide

analysis of the daily cycle of HNO_3 that suggests this estimate of the HNO_3 lifetime is too long (perhaps because the deposition velocity is closer to 0.05 m/s). During the daytime, the HNO_3 concentration is observed to be nearly in a chemical stationary state with a production term characterized by R_S and loss to deposition. This would not be the case if the time scale for production and deposition were much longer than 3 hours. This result implies that more than 70% of the HNO_3 formed during transit from Sacramento to Tahoe is deposited along the western slope of the Sierra Nevada. This short lifetime suggests that attention be focused on the controls over NO_2 mixing ratios in the Tahoe basin (or anywhere else where dry HNO_3 deposition is a potential problem). The deposition velocity of ammonia is similar to that of HNO_3; thus, we can make similar assumptions about its lifetime in the plume. Since NH_3 is a primary pollutant, its concentration $[X]_S$ should start decreasing immediately as the airmass moves away from the emission source. Under cool or humid conditions, the formation of NH_4NO_3 particles could prolong the lifetime of these forms of inorganic nitrogen because accumulation-mode sized particles deposit less quickly than gas phase compounds. Warm daytime temperatures in summer favor gas phase species but aerosol may be important in the winter or at night.

Organic Nitrate (RO_xNO_2) Formation

Other photochemical byproducts that act as a sink or reservoir for NO_x include peroxy nitrates and alkyl nitrates formed by the reaction of RO_2 with NO_2 and NO respectively. In the concentration range of NO_x encountered outside urban areas, organic nitrates can be the major sink of NO_x radicals. While HNO_3 forms efficiently under high NO_x conditions, RO_xNO_2 formation becomes more favorable as the NO_x to hydrocarbon ratio decreases. The lower deposition velocity of organic nitrates lengthens their lifetime in the plume but also makes them less efficient as a source of atmospheric nitrogen to the surface. Hydroxy alkyl nitrates are expected to have comparable deposition velocities to HNO_3, but it is unclear what fraction of organic nitrates these comprise. Peroxy nitrates are thermally unstable and therefore capable of sequestering NO_x under cold conditions and releasing it once temperatures rise. This can be an effective mechanism for transporting reactive nitrogen to distant places. Observations by *Day et al.* [2003] at UC-BFRS show that for many parts of the year, the sum of all organic nitrate

species is often the most significant fraction of NO_y in the plume by the time it reaches the site. More needs to be known about the behavior of these species to assess their potential to deliver reactive nitrogen to Lake Tahoe. Note that atmospheric chemists refer to $RONO_2$ and RO_2NO_2 collectively as 'organic nitrates'; a term that should not be confused with 'organic nitrogen', which is used to refer to compounds with a C-N bond. Little is known about the aqueous decomposition of peroxy and alkyl nitrates, and whether their NO_3 group would contribute to nitrate measurements in analysis of lake water or precipitation. Just as the effective Henry's Law constant of HNO_3 is increased by its subsequent hydrolysis in solution, hydrolysis increases the solubility of peroxyacetyl nitrates, but their loss remains orders of magnitude lower than HNO_3. The Henry's Law constants for these organic nitrates are generally low (1-4 M atm^{-1}) and subsequent (pH-dependent) hydrolysis increases their uptake; studies show that the deposition velocity over a stagnant water surface is hydrolysis rate limited [*Kames and Schurath*, 1995; *Kames et al.*, 1991]. Measurements of the effective Henry's Law constants of hydroxy- and multi-functional alkyl nitrates (6000 – 40 000 M atm^{-1}) approach the value for HNO_3 and suggest that some alkyl nitrates will partition effectively into the aqueous phase [*Kames and Schurath*, 1992; *Shepson et al.*, 1996; *Treves et al.*, 2000]. The solubility and deposition rate of long straight chain alkyl is considerably lower, so the contribution of the $RONO_2$ class depends strongly on the balance among species with different R groups.

Downwind emissions

The Lagrangian analysis by *Dillon et al*. [2002] of nitrogen oxides at UC-BFRS indicated that emissions into the urban plume continue after it passes over Folsom. These emissions are large ~0.44 ppb/hr. After the five hours of travel on the way to UC-BFRS, the total emissions are 2.2 ppb, an amount in excess of the background concentration observed at the site and fully 2/3 of the amount observed at the peak of the urban plume. This result strongly implies that transportation along the major highway corridors (50 and 80), contribution from housing beyond the edge of the Sacramento suburbs and direct emissions from the local ecosystems are significant contributors to NO_y in the Sierra. Recent improvements to the model, which include a time-dependent treatment of organic nitrates, suggest that these values for downwind emissions

may be overestimates. Further research is needed to identify the sources and magnitudes of fresh emissions of NO_x in the region.

Summary of plume transport and chemistry

The above analysis makes use of a continuous long term dataset that allows for the evaluation of statistics. This comprehensive record of meteorology and chemical composition at UC-BFRS is consistent with other observations from the western slope of the Sierras including aircraft measurements, data from Big Hill (1850 m), and short term ozone studies. Using a model that accounts for the combined effects of emissions, chemistry, deposition and dilution which can be tested against an inclusive set of observations allows us to develop an representation of the mean behavior of NO_y species in the region. The influence of the urban plume causes an increase in the typical daytime peak mixing ratio of NO_y at UC-BFRS, which occurs just prior to sunset, to near 3.3 ppb, an amount that is 1.4 ppb above the regional background of 1.9 ppb. For most of the day, the observed mixing ratios are much less than this peak value with a daytime average concentration of about 2.5 ppb (0.6 ppb above the regional background). Thus on an average day at UC-BFRS, the contribution of the urban plume raises the diurnally averaged NO_y by 32% over the background. Assuming the Lagrangian parameters represent transport beyond UC-BFRS, then further dilution and deposition of HNO_3 along the plume's trajectory to the Lake will mean an even lower contribution of NO_y from the urban plume to the Tahoe basin.

At least as important as the total amount of NO_y transported within the plume, is the change in species distribution as the plume evolves. HNO_3 dominates the higher oxides of nitrogen (NO_z) near emission sources of NO_x but is rapidly lost if the airmass remains in contact with the surface. On the other hand, the plume becomes relatively enriched in organic nitrates as it progresses through the day with the sunlight driving hydrocarbon oxidation, creating RO_2 radicals to combine with the NO_x in the plume. These hydrocarbons have both anthropogenic and biogenic sources. If nitrogen oxides emitted in the Valley do reach the Tahoe Basin, it is likely they will make it there in the form of organic nitrates. Production of fine particles (<2.5 μm aerodynamic diameter) containing nitrate may be another mechanism for transporting reactive nitrogen, as this size of aerosol has a substantial lifetime (hours-days) in an airmass.

The direct extrapolation of the plume analysis presented above in order to understand inputs to Lake Tahoe is only accurate if the upslope flow is strong enough and persistent enough to deliver air from the Central Valley to the Tahoe Basin in one day. If an average daytime wind speed of 3.5 m/s is used, it would be possible for an airmass to leave Sacramento at 10 am and travel 130 km east to the Tahoe Basin by 8 pm that night. Using appropriately timed NO_2, NO_x, and NO_y observations from monitoring sites along the Sacramento-Tahoe transect in July enables us to examine the evolution of reactive nitrogen in the plume (Figure 6). As described above, as the plume moves away from Sacramento and ages, the abundance of reactive nitrogen decreases as the result of dilution, processing and deposition. However, NO_x observations at South Lake Tahoe are substantially higher than one would expect from an extension of the values at UC-BFRS and Big Hill, suggesting a substantial contribution from local in-basin emission sources.

Limited aircraft measurements of HNO_3/NO_3^-, NH_3/NH_4^+, and organic nitrogen in the gas and particle phase have been made in the Tahoe Basin and at low and mid-elevation sites along the western slope of the Sierra Nevada [*Zhang et al.*, 2002]. While the abundance of these species is significantly lower in the Basin than on the Western slope of the Sierras, the distribution between the species was found to be similar in all locations. The authors infer from these observations that under summertime meteorological conditions, Central Valley emissions can be a significant source of nitrogen to the basin. However, because the timescale of photochemistry and deposition of the nitrogen oxides is short, we expect the distribution among different classes of NO_y to have strong variations depending on the time of day and proximity to the source, but not necessarily the identity of the source. Further, if the Central Valley was the main source of HNO_3 and NH_3 for all the sites, because Tahoe is further along the transect than the lower elevation sites, one might actually expect a very different N distribution. Additionally, there may be some bias resulting from the timing of the measurements: all the western slope measurements occur between noon and 4 pm while half of the Tahoe Basin measurements are in the morning. These intermittent observations are not sufficient to address the issue of transport from the western slope into the basin.

IIIb. Other transport paths

The typical ground level monitoring network does not effectively characterize air pollution transport aloft (Arrows 2-3 in Figure 1). It is possible that air with high concentrations of nitrogen oxides is lofted well above the surface in the Central Valley and then transported to the east without further contact with the surface until arriving in the high Sierra or the Tahoe basin itself. Air that does not contact the ground would not be subject to the same deposition losses as that within the planetary boundary layer. However, there is no evidence to suggest that this is a mechanism for persistent and effective transport. Although there are some aircraft and ground-based data that suggest high concentrations of pollutants can be trapped above the nocturnal boundary layer in the Sacramento region [*Carroll and Dixon*, 2002], the same aircraft data show that the plume does not travel east into the Sierra Nevada beyond the ridges at about 2000 m ASL. Aircraft observations made above the Lake suggested that conditions of neutral stratification over the lake promote vertical mixing, which would enable pollutants passing over the lake at high altitudes to mix downwards, but would also result in significant dilution. A more quantitative approach is required to assess the probability that air from the west passes over the Sierra crest to Lake Tahoe and penetrates the mixed layer over the lake surface (following Arrows 2,3 and 5), thus permitting dry deposition of atmospheric nitrogen from sources upwind of the basin.

IIIc. The regional background

Recent surface and aircraft observations in the lower 5 km of the troposphere suggest that airmasses arriving at the California coast contain less than 0.5 ppb of NO_y prior to the addition of continental emissions [*Hudman et al.*, 2004]. The background concentrations of NO_y observed at UC-BFRS, which evidence suggests is widespread in the foothills of the Sierra Nevada are significantly higher, and are likely the major component of surface nitrogen oxides $[X]_s$ that may enter the Tahoe basin from the west. The regional background along the western slope of the Sierras is strongly affected by the recirculation of airmasses (Arrow 4 in Figure 1) resulting from the upslope/downslope pattern. Even on days when the urban plume does not reach Lake Tahoe, the reactive nitrogen contained within it may remain in the Sierras and contribute to increased

background levels of atmospheric nitrogen and enhanced deposition. However, nighttime gas phase and heterogeneous chemistry may remove nitrogen oxides before the following day. The broader influence of the emissions from Sacramento and the Central Valley depends on the synoptic weather patterns and the distribution of reactive nitrogen among its constituent compounds. In the summer, net air flow is from the west and emissions from the Central Valley can accumulate along the western slope of the Sierra and ultimately affect the Tahoe Basin. In the winter, observations at UC-BFRS and at Camino, along Highway 50, suggest that the net air flow at the surface is actually from the east (Figure 7). This is consistent with much lower background values of NO_y during the colder season, and suggests that emissions from the west do not undergo net transport toward Tahoe in the surface layer during the winter. Observations to date do not provide an adequate explanation for the observed background and further research is needed.

IIId. Burning

Forest fires and biomass burning are recognized to have significant effects on nearby ecosystems. Efforts have been made to characterize and quantify the pyrogenic emissions from various fuel sources [*Andreae and Merlet*, 2001]. Studies of biomass burning plumes have identified elevated levels of many reactive nitrogen species and observed a change in NO_y partitioning as the plume aged [*Mauzerall et al.*, 1998]. Another study noted an increase in nitrate-containing particles as the smoke aged over the first hour [*Hobbs et al.*, 2003]. Zhang et al. [2002] intercepted a forest fire plume during flights over the northern edge of the Tahoe Basin and observed elevated concentrations of reactive nitrogen 35 km downwind of the fire. The observations also demonstrate an enrichment in organic nitrogen in the particulate phase, consistent with the nitrogen partitioning observed another day in slightly smoky air over Lake Tahoe. Burning may not only liberate additional nitrogen oxides into the atmosphere, but also lead to a redistribution of the species, affecting the deposition rate of nitrogen to the lake

Both wildfires and prescribed burning events occur in the region, typically in the late fall/ early winter. While hot, dry conditions, often associated with easterly winds, may lead to wildfires, prescribed burning events are, for this very reason, more likely to take place under cool wet conditions. Though the prevailing wind conditions during this season do not favour long

range net upslope transport along the western Sierra (Arrows 1 & 4 in Figure 1), if the fire is sufficiently close to Lake Tahoe, there may be sufficient time for the associated emissions to reach the Tahoe Basin. The temperature and humidity will also play important roles in determining the influence of emissions from burning events of nearby ecosystems. Nitrogen contained in large particles (> 10 μm) and soluble gases (i.e. HNO_3 and NH_3) deposit quickly, whereas the timescale for dry deposition of fine particles is several days and they may therefore have a larger geographical extent of influence. Studies have shown that fire-generated particles exist primarily in the accumulation mode, with diameters less than 2μm, are composed mainly of organic fraction, and often contain substantial amounts of inorganic nitrogen [*Kleeman et al.*, 1999]. Experimental burns carried out in Arizona on grassland and ponderosa pine (a common species in the western Sierra) measured fresh plumes (age ~ 10 min) and showed that the chemical composition of the emissions depended strongly on the fuel type and phase of the fire (flaming or smoldering) [*Robinson et al.*, 2004]. Data obtained at suburban monitoring stations downwind of summer forest fires in Montana show that the total amount of $PM_{2.5}$ was a factor of five higher than regular summertime measurements, but only slightly higher than average wintertime concentrations [*Ward et al.*, 2004]. Compared to summertime urban aerosols, the nitrate concentration during fire events was a factor of four higher, and the ammonium concentration was 50% higher. As prescribed burning events on the western slope of the Sierra often occur later in the year, partitioning of gas phase nitrogen species into the aerosol phase is likely to be favoured. In order to assess the contribution of burning events to the nitrogen oxides in the Tahoe Basin, a detailed inventory of burning frequency, intensity and location is required, in conjunction with detailed knowledge of temperature and wind patterns.

IV. Wet Deposition of Nitrogen within the Tahoe Basin

Few studies have addressed wet deposition, which occurs mainly in the winter, and at high elevations is generally the result of snow rather than rain. The contribution of wet deposition to total N deposition within the Tahoe Basin cannot currently be quanitified, because no studies have measured gas and aerosol phase nitrogen in the atmosphere and in precipitation on a year-round basis. Wet deposition of N contributes nutrients to Lake Tahoe when falling precipitation delivers nitrogen to the surface of the Lake (or basin with subsequent runoff into

the lake). The source of the nitrogen in the precipitation is difficult to determine, as it may have existed within clouds prior to their arrival in the region, accumulated as the cloudwater was advected over continental areas with anthropogenic emissions, or been scrubbed from the local atmosphere as the precipitation falls to the surface. With reference to Figure 1, the concentration of N in global background precipitation is depicted as concentration A. Airmasses moving from west to east along Arrow 3 incorporate regional emissions of reactive nitrogen (NO_y and NH_3) whose concentration in the free troposphere, $[X]_F$, are determined by emissions, mixing and chemical processing. As the airmass continues to be advected along 3, physical and chemical parameters determine the extent to which reactive N becomes incorporated into cloudwater or precipitation. To our knowledge, no measurements of the N content of precipitation aloft (concentration B) over the Sierra Nevada have been made. Wet deposition leads to N inputs into Lake Tahoe if precipitation events occur as the airmass is over the Tahoe Basin. As the precipitation falls through the atmospheric boundary layer over the Basin, soluble forms of nitrogen with concentration $[X]_T$ are scrubbed from the atmosphere resulting in concentration C. Observations of the NO_3^- and NH_4^+ content of precipitation in the Tahoe Basin (representing concentration C) by Jassby et al. [1994] and observations of atmospheric concentrations of soluble forms of N allow us to estimate the relative contributions of in-basin nitrogen sources to the wet deposition of nitrogen to the surface of Lake Tahoe.

Jassby et al. record dry and wet N deposition data for a station at Ward Creek, and an east-west transect across the lake. They observe that NH_4^+ and NO_3^- are the dominant forms of N in wet deposition, and they estimate that the average deposition across the basin is half the deposition at Ward Creek. This estimate is supported by measurements over several years by Melack et al. [*Melack et al.*, 1997] of nearby alpine snowpacks which found 2240-5370 $\mu mol/m^2$ NO_3^- and 2160 to 5840 $\mu mol/m^2$ NH_4^+ prior to spring snowmelt. They note that much of the variability is derived from the timing of the precipitation events.

Data from in Jassby et al. (i.e., Tables 1 & 7) was used to compile the table below, which documents the average precipitation each year and the average amounts of NO_3^- and NH_4^+ found in the precipitation. The difference is the excess of nitrate, which could result from wet deposition of gas phase HNO_3 or wet deposition of other nitrate salts such as $Ca^{(}NO_3)_2$ in the precipitation.

Table 1. Precipitation Volume and Inorganic Nitrogen Content for a Tahoe Basin Site

Year	Precipitation (m)	NO_3^- (μmol/m^2 year)[*]	NH_4^+ (μmol/m^2 year)[*]	Difference (μmol/m^2 year)	Ratio
1989	1.20	3650	3176	474	1.15
1990	0.785	3960	3650	310	1.08
1991	0.75	2573	2080	493	1.24
1992	0.653	2354	1790	564	1.32

*multiply (mmol/m^2 day) at Ward Creek by 365 days and divide by 2 for basin average

If we assume that all the nitrogen deposited at the Lake was contained in the precipitation before it entered the basin (i.e. concentration B), this would require snow or rain with 3.0, 5.4, 3.4, 3.6 μM concentrations of NO_3^- and 2.6, 4.6, 2.7, and 2.7 μM NH_4^+. This is similar to precipitation falling over the 1200-1800 m elevation range in Washington's Cascade mountains, which had an average wintertime nitrate concentration of 3.2 μM [*Duncan et al.*, 1986]. Comparison of these concentrations to remote sites allows us to estimate the effect of upwind or local emissions. Between 1993-1996, precipitation over a montane forest in Hawaii [*Heath and Huebert*, 1999] had an average [NH_4NO_3] of 1.5 μM, and NO_3^-:NH_4^+ ratios ranging between 1.0 and 1.4, similar to Tahoe. In another study, over Bermuda in 2000, nitrate concentrations ranged between 1.4 μM for airmasses originating over the ocean up to 16.8 μM for back-trajectories which originated over continental USA[*Hastings et al.*, 2003]. Precipitation that develops over clean marine areas has NH_4NO_3 below 2 μM so it is likely that regional or in-basin anthropogenic emissions contribute partly to the N content of precipitation in the basin.

To estimate the potential contribution of in-basin atmospheric nitrogen to wet deposition, we consider the wintertime meteorology and chemistry. Over 90% of precipitation over Lake Tahoe falls between October and May, when the average

maximum and minimum temperatures are below 10 °C and 0 °C. Under these conditions and at high relative humidity, gas phase HNO_3 and NH_3 partition strongly into the aerosol phase. NH_4NO_3 particles smaller than 2.5 μm have relatively slow deposition velocities (< 1 cm/s) and can persist for days in the atmosphere. Analysis of IMPROVE data for Bliss and South Lake Tahoe show that NH_4NO_3 at the two sites are almost equal during summer, but South Lake Tahoe has substantially more nitrate aerosol than Bliss from October through April. A possible explanation for this wintertime gradient is that a combination of low mixing heights and frequent precipitation during the winter prevents the aerosol from mixing throughout the basin and results in higher concentrations closer to sources of NO_x. Because of the low temperatures, and the fact that NO_3^- is consistently higher than NH_4^+, equilibrium requires that average basin-wide gas phase NH_3 is negligible during the winter months, and we assume that NH_4^+ is equimolar to NH_4NO_3. An upper estimate of $[X]_T = 500$ ng/m^3 is reasonable for both aerosol NH_4NO_3 (0.16 ppb) and gas phase HNO_3 (0.20 ppb) averaged over the Lake Tahoe Basin. If the atmosphere is well-mixed to a height of 1 km above the lake surface, and the precipitation falls through this 1 km, completely scrubbing the aerosol and gas phase concentrations of 500 ng/m^3 NH_4NO_3 and HNO_3, then every m^2 of lake surface would receive 6.25 mmol of NH_4NO_3, and 7.9 mmol of HNO_3. As an upper limit, if 50 non-consecutive precipitation days were possible in a year, with the atmosphere recovering its concentrations of NH_4NO_3 and HNO_3 between each event, then 300 mmol/m^2 of NH_4NO_3 and an additional 400 mmol/m^2 of HNO_3 could be deposited annually. This conservative estimate contributes only 10-20 % of the observed wet deposition of nitrogen in the basin. The difference between the observed annual rates

of wet N deposition and the amount contributed by in-basin inorganic nitrogen and the global background present in 'clean' rain can likely be attributed to incorporation of atmospheric nitrogen into the cloud chemistry on the path from a meteorological marine front, through coastal and urban areas, and finally ending in alpine precipitation. A recent modeling study integrating multiphase chemistry and microphysics has shown that during cloud and precipitation formation pernitric acid is taken up by the water and converted to nitrate [*Leriche et al.*, 2003]. Because NO_2 is in thermal equilibrium with pernitric acid, this results in a mechanism whereby upwind sources of atmospheric NO_x can be efficiently transferred into precipitation to form soluble nitrate (during transit along Arrow 3). Roughly 50 % of the inorganic nitrogen in precipitation over Lake Tahoe should be considered global in character (concentration A), with another 30-50 % contributed by incorporation of regional/continental N emissions, and likely a small 0-20 % contribution to the final concentration C from the uptake of soluble N from local in-basin sources by falling precipitation. To accurately quantify these contributions, gas and aqueous phase measurements of soluble N-containing compounds must be made in the troposphere upwind of Lake Tahoe during the winter. It should be noted that winter precipitation in the Tahoe Basin has only twice the nitrate observed at remote locations, whereas many sites in Asia, Europe, and the United States have nitrate levels at least an order of magnitude higher.

V. Summary

In addition to local sources of reactive nitrogen to the Tahoe Basin, other potential upwind sources include emissions from the Sacramento urban area, industrial and agricultural

activity in the Central Valley, transportation along highway corridors, biomass burning and biogenic emissions from ecosystems within the western Sierra Nevada. The ability of these emissions to affect the water quality of Lake Tahoe depends on their chemical processing and on the transport pathways that bring the air toward the Tahoe Basin. Analysis of long term ground level observations suggest that most HNO_3 within the urban plume deposits prior to reaching Lake Tahoe, though organic nitrates may persist. Short-term aircraft studies attempting to identify transport pathways for pollutants have occasionally observed higher concentrations of photochemical products lofted above the mixed layer. Downwind of biomass burning episodes, elevated levels of reactive nitrogen in both the gaseous and particulate phase have been observed [*Zhang et al.*, 2002]. If these burning events occur within five hours transit time to the Tahoe Basin, they may be capable of delivering additional nitrogen to the atmosphere above the Lake. Our best estimate is that wet deposition (which Jassby [1994] approximates as half the source of N to the lake) derives 50% its nitrogen content from the global background, 10-20% from local in-basin sources and the remainder from other sources, possibly to the west of the basin. More quantitative research is needed to understand the flow dynamics within the Tahoe Basin that would permit better characterization of vertical mixing processes and improve estimates of reactive nitrogen dry deposition to the lake.

VI. Key Research Issues

To ascertain whether reactive nitrogen emissions from upwind air basins contribute to nitrogen deposition in the Lake Tahoe basin, a spatially and temporally comprehensive representation of the atmospheric chemistry and dynamics of the region is required. Nitrogen deposition is a chronic problem, in contrast to extreme events such as exceedances of the O_3 standard, and requires collection and analysis of longterm data sets. The chemical species involved: NO_x, organic nitrates, HNO_3, NH_3, and NH_4NO_3 have lifetimes on the order of hours to days, which means that both daily and synoptic weather patterns in the area must be considered. Both gas phase and aerosol species must be measured, and a complete understanding requires consideration of both dry and wet deposition.

There are essentially two linked but separate questions that need to be addressed:

1) What is the nitrogen flux to the Tahoe basin and subsequently to the surface of Lake Tahoe?

2) What are the sources of the nitrogen species that deposit onto surfaces within the basin?

Answering the first question requires sensitive, high time resolution measurements of meteorological parameters and the above-mentioned species throughout the Lake Tahoe basin, including NO_3^- and NH_4^+ measurements in precipitation during rain/snow events. This will enable quantification of mechanisms for nitrogen transfer to the Lake including both direct atmospheric deposition to the Lake and atmospheric deposition to other basin surfaces followed by runoff with high N-content.

The temporal and spatial variability in this data can be interpreted to give some indication of the sources of reactive nitrogen to the basin. Also, measurements made upwind of the basin can be used as a boundary condition on the total amount of reactive nitrogen available in upwind airmasses before they enter the Lake Tahoe basin. Data collected at sites on the western slope of the Sierra Nevada suggest that the transit time of a boundary layer airmass from Sacramento to Lake Tahoe generally exceeds the period of upslope flow during a summer day. This implies that if upwind reactive nitrogen emissions from urban areas have any impact over Lake Tahoe, then it is through an increase in the regional background. The lifetime of reactive nitrogen is largely determined by the deposition rates of its constituent members. Organic nitrates and NH_4NO_3 aerosol (PM 2.5) are longest-lived and therefore most likely to persist in the background, but, because of their correspondingly slow deposition rates, they are also the least likely to deposit to the lake surface. Thus, it is easy to imagine a scenario in which the majority of reactive nitrogen in an airmass over Lake Tahoe has its origin in aged Sacramento emissions but the recent in-basin emissions of NO_x, quickly oxidized to HNO_3, are what actually deposits

to the lake surface.   This underlines the need to obtain high time resolution, spatially comprehensive observations of all the members of the reactive nitrogen family if the goal is to quantify deposition AND ascertain the source of the deposited nitrogen.

To more quantitatively assess the contribution of in-basin and out-of-basin nitrogen sources it is necessary to improve our understanding of:

- the total amount of atmospheric deposition to the basin, both directly to the lake surface, and to other areas of the basin that capture nitrogen with subsequent transport to the lake

- the relative contributions of wet and dry deposition

- the importance of burning events on the western slope based on emissions and meteorology

- the deposition rates of all atmospheric forms of N, including HNO_3, NH_3, NH_4NO_3, organic nitrates (RO_xNO_2), and organic nitrogen (C-N bonds)

- the extent to which N is removed during transport along the western slopes of the Sierra in each season

- the characteristics of N in the regional background

- the amount of N emitted by the forests of the Sierra

- the sources of N in rain and snow

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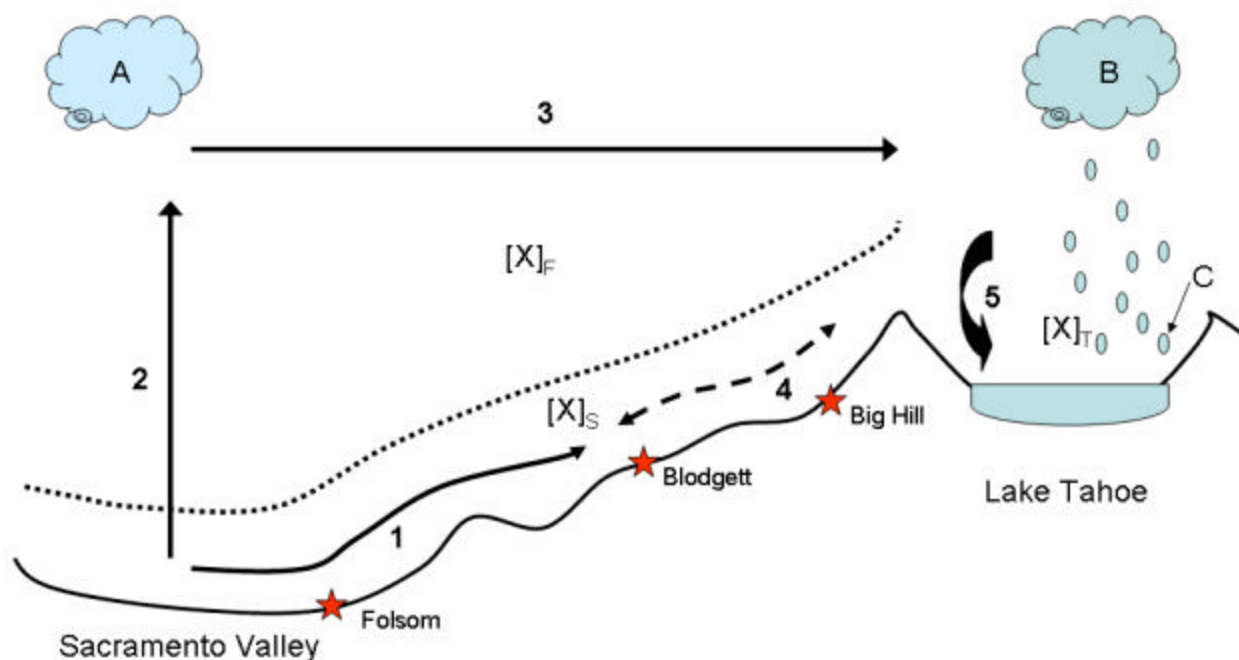
Figure 1. Schematic of possible transport paths between the Sacramento Valley and the Lake Tahoe Basin relevant to dry and wet deposition. The dotted line represents the upper boundary of the surface or planetary boundary layer. Emissions from the Sacramento Valley may be transported eastward along Arrow 1: direct transport within the boundary layer, which occurs upslope during the day and Arrow 4, which is dotted to represent our uncertainty regarding the easterly extent of this flow on any particular day, or on average. Arrows 2 and 3 show lofting of the airmass above the valley floor and subsequent advection to the east. Arrow 5 represents vertical atmospheric mixing over the lake, which must occur in order for reactive nitrogen that reaches the Basin under either advection scheme from the west to undergo dry deposition to the lake. Red stars indicate measurement sites along the Sacramento – Tahoe transect that are used in this analysis.

Urban emissions increase the concentration of a compound in the surface layer $[X]_S$, which can undergo subsequent photochemistry, mixing and deposition as the airmass is advected along Arrows 1 and 4. Urban emissions may be lofted directly (Arrow 2) to increase concentrations in the free troposphere, $[X]_F$. As the airmasses are advected, if $[X]_S$ is greater than $[X]_F$, mixing between the surface layer and the free troposphere will increase concentrations in the free troposphere and reduce them in the surface layer (and vice versa). The atmospheric concentration of a compound in the Lake Tahoe Basin $[X]_T$ is determined by $[X]$ in the incoming airmass and the strength of the in-basin emissions.

Wet deposition is another mechanism whereby nitrogen can by added to the Lake Tahoe Basin. Cloud A represents the nitrogen content measured in clean or remote regions that can be seen as a global background. As the airmass is advected over an area with significant emissions of reactive nitrogen $[X]_F$ will increase and the equilibrium between concentrations in the atmosphere and the cloudwater will increase the N content to that represented in Cloud B, which

now also has a regional contribution. If a precipitation event occurs over the Tahoe Basin, the falling rain or snow will start out with concentration B, but for all soluble compounds, $[X]_T$ will become incorporated in the falling precipitation so that the N content of the wet deposition at the lake surface is represented by C.
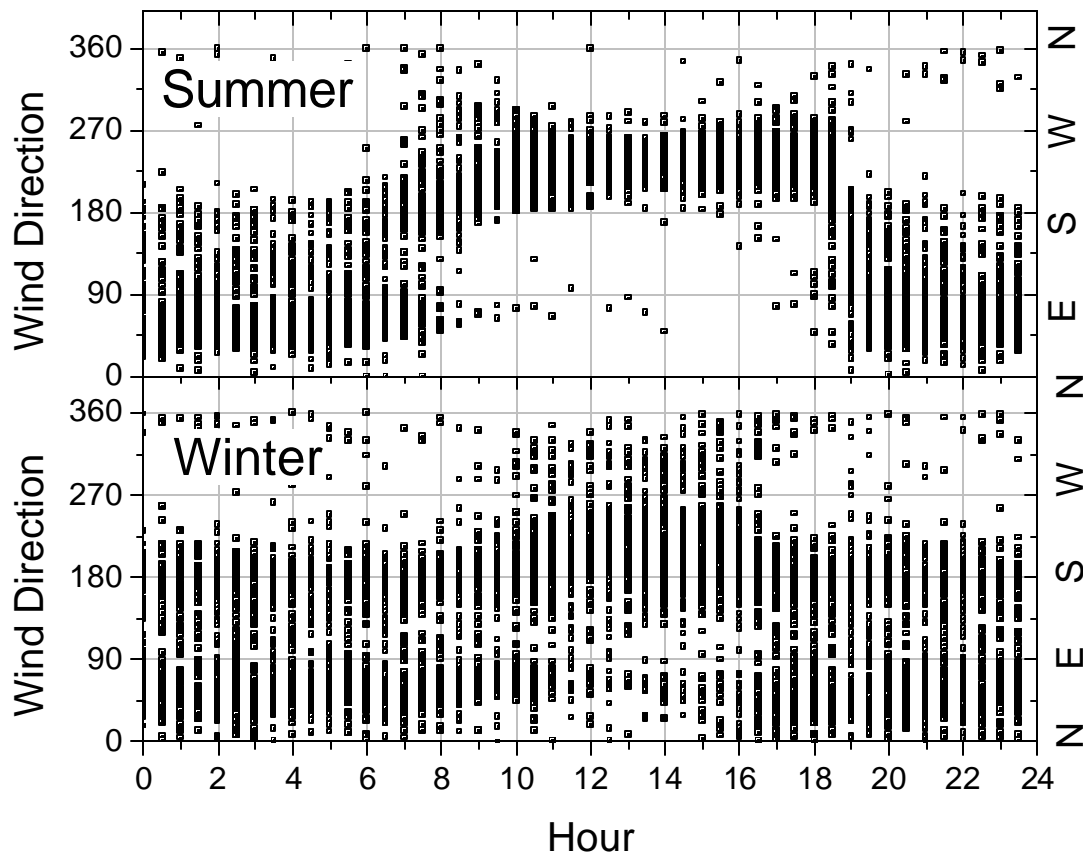

Figure 2. Half hour averages of wind direction observations at Blodgett Forest during 2001. Summer refers to data between day 155 and 255 (June 5- Sep 12) and winter refers to data before day 50 (Feb 20) and after day 300 (Nov 2).
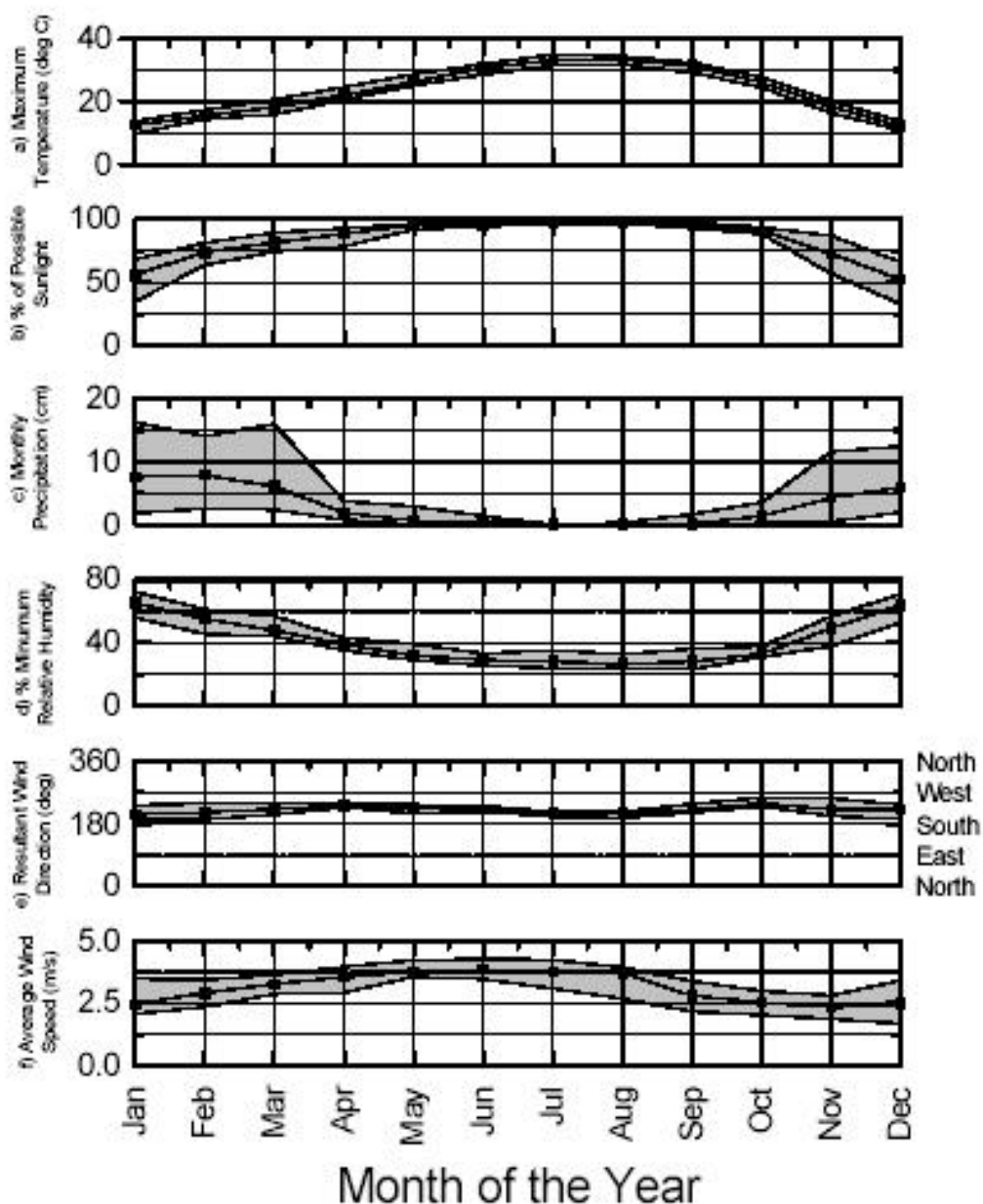
Figure 3. Monthly averaged observations at the Sacramento Executive Airport (WBAN 23232) demonstrate the inter- and intra- annual variance of climatological variables in the region from 1980 through 1999. The line with solid squares is the median of monthly means while the gray swath denotes the 1s variance. a) maximum daily temperature; b) percent of total possible hours of direct sunlight (no observations were available in 1998 and 1999); c) sum of monthly rainfall; d) the lowest relative humidity recorded each day (typically a late afternoon observation); e) daily origin direction of 24 hour average of recorded winds (also called resultant wind direction); f) 24 hour average of recorded wind speeds.

Figure 4. Major roads and 1998 California Air Resources Board atmospheric sampling sites upwind of the Blodgett Forest Research Station: Photochemical Assessment Monitoring Station sites (circled P), co-located ozone, nitrogen oxide and non-methane hydrocarbon monitors (+), co-located ozone and nitrogen oxide monitors (star), and ozone monitors (diamond). Most observations used in this study were taken from the Blodgett Forest Research Station, Del Paso Manor, and the Folsom sampling sites.
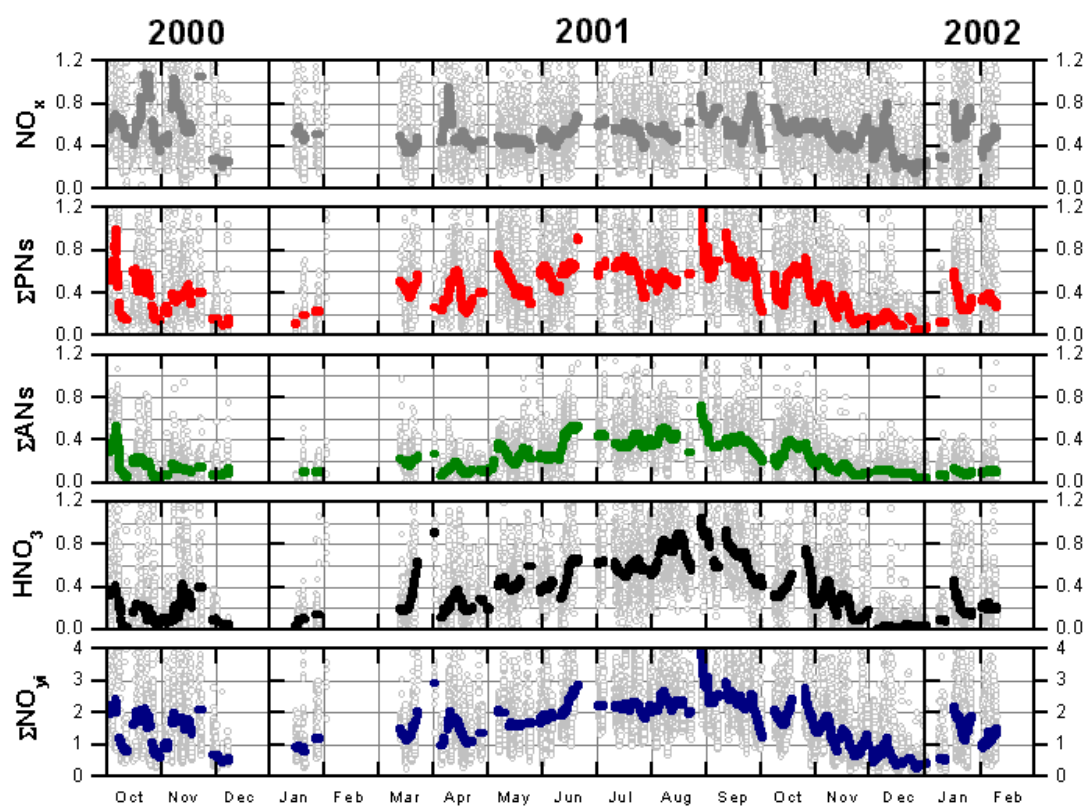
Figure 5. Observations of nitrogen oxides (ppbv) at UC-BFRS 2000-2002 (30-minute averages and 7-day running medians)
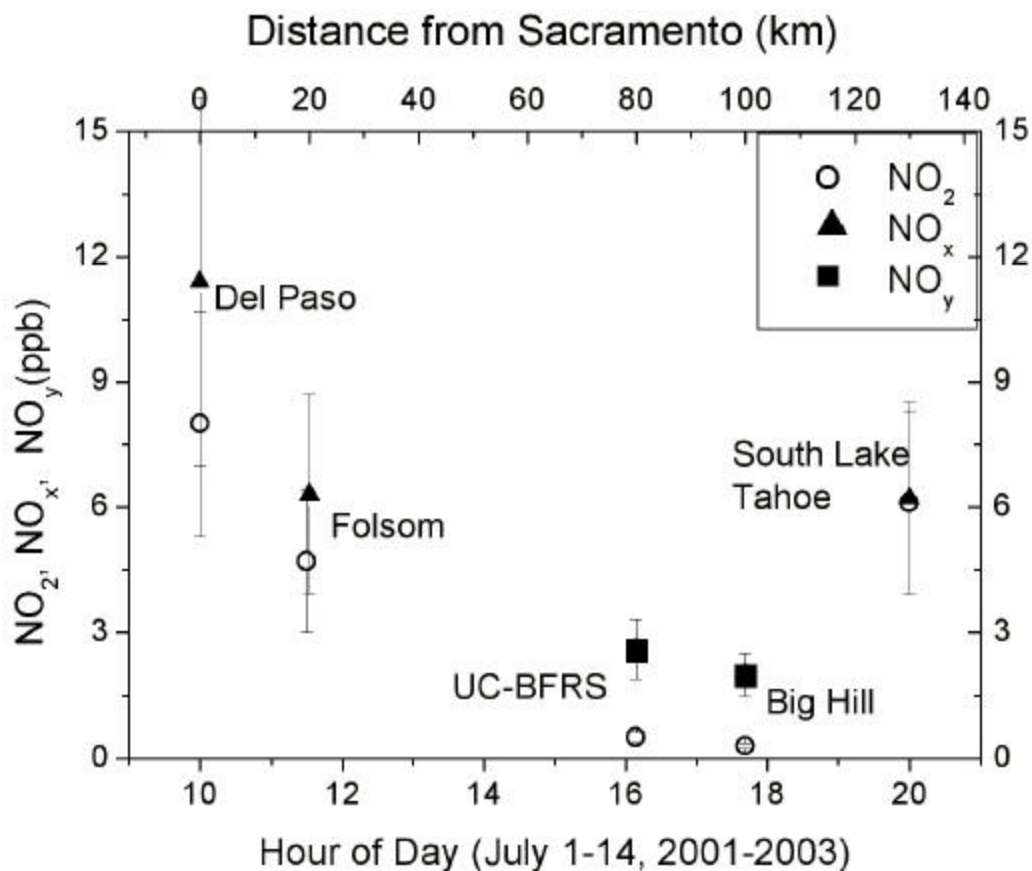
Figure 6. Reactive nitrogen observations along the Sacramento-Tahoe transect. The distance from Sacramento was multiplied by an average wind speed of 3.5 m/s [Dillon 2002] to estimate the time the airmass would arrive at each site after leaving Del Paso at 10 am. Observations at each site were averaged for an hour around the estimated time. For example, UC-BFRS lies 80 km downwind of Del Paso, and NO_2 and NO_y observations between 3 pm and 5 pm were averaged to produce the points reported at 4 pm. The error bars represent the standard deviation of the average.
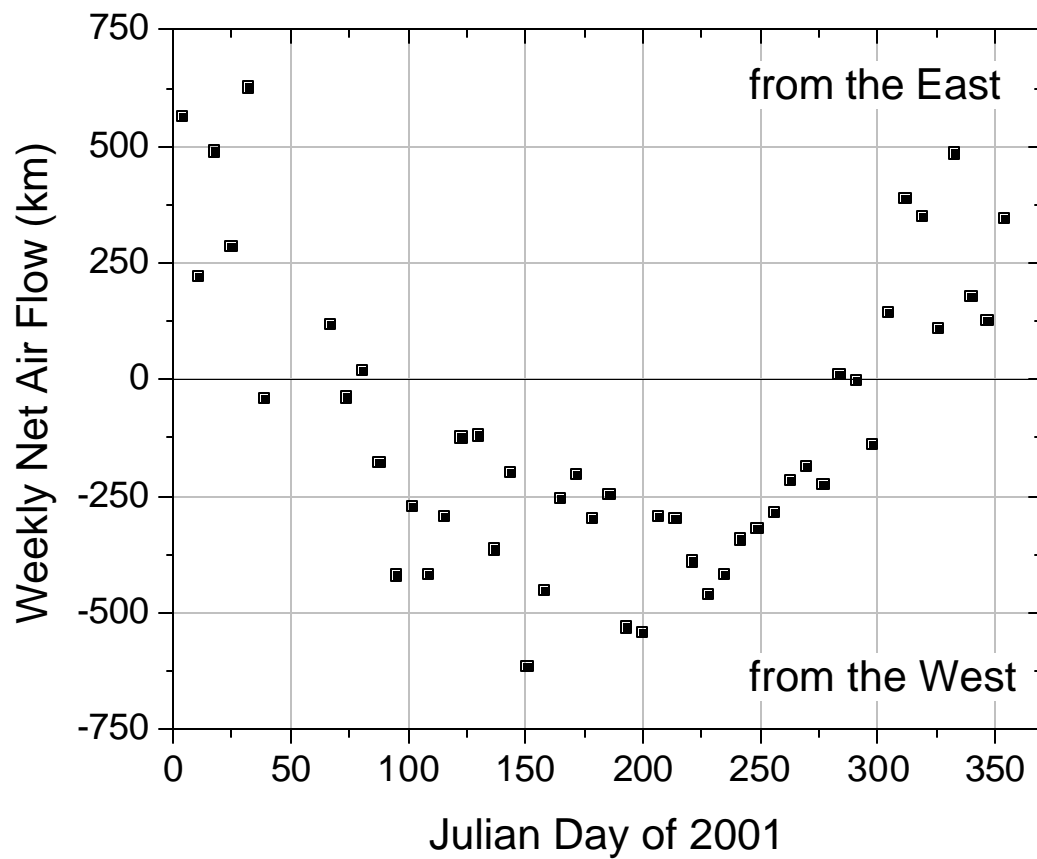
Figure 7. Weekly averages of net east-west air flow throughout 2001 using wind speed and direction data from a 10m tower at Blodgett Forest (1400 m) elevation on the western slope of Sierra Nevada.